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(54) **Improved methods and composition for making a pressure sensitive adhesive coated laminate**

Verbesserte Verfahren und Zusammensetzung zur Herstellung eines mit einem druckempfindlichen  
Klebstoff beschichteten Laminates

Méthodes améliorées et composition pour fabriquer un stratifié revêtu d'un adhésif agissant par  
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**WO-A-87/03537** **GB-A- 1 541 311**  
**US-A- 4 151 319** **US-A- 5 082 706**

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## Description

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

[0001] This invention pertains to the field of laminates having an improved pressure sensitive adhesive layer. More particularly, this invention relates to the method of making improved pressure sensitive adhesive coated laminates for covering substrates for decorative and/or protective purposes or for adhesive tapes, labels, and the like.

## 2. Description of the Prior Art

[0002] The development of pressure sensitive adhesive systems has resulted in their use in a great variety of areas, such as, for tapes, decals, decorative and protective coverings in sheet form for walls, furniture, and the like, self-stick floor coverings, and generally, for any purpose wherein it is desired to adhere an article to a substrate.

[0003] Because of the increased movement towards the so-called "do-it-yourself" type of home improvements and decorating, many articles, such as, wall coverings, counter coverings, tile appliques, shelving covers and edgings, and the like, are now sold with pressure sensitive adhesive coatings thereon. Such pressure sensitive adhesive coatings facilitate the application of such articles to the desired substrate by eliminating the need to apply a separate adhesive or to utilize another type of securing device, such as nails, screws, staples, etc.

[0004] One of the problems with such pressure sensitive adhesive coated articles is that, in use, they are extremely difficult to position and, if necessary, reposition, even immediately after the application to the substrate. This problem is particularly severe with articles which are in the form of decorative and protective sheets coated with a pressure sensitive adhesive, and which are used to cover substrates, e.g., walls, cabinet tops, furniture, etc. Very often, such sheets or laminates possess decorative patterns on the outer face and it is important that the proper matching of the patterns from adjacent sheets be obtained. Moreover, it is often important that the seams between adjacent sheets be straight, uniform, and parallel.

[0005] Another problem which arises, particularly with larger pieces or sheets, such as, when one is attempting to cover a large piece of furniture or large wall area, is the difficulty in handling the sheet and the avoidance of touching of one area of the pressure sensitive adhesive coated side of the sheet with another area of the same side. When this occurs, the sheet will fold and the respective touching areas must be pulled apart. This can become extremely cumbersome, particularly with large sheets.

[0006] It also can result in removal of areas of the pressure sensitive adhesive coating when an attempt is made to pull the touching areas apart and cause discontinuities of the pressure sensitive adhesive coating as well as produce torn, stretched or wrinkled areas in the facing sheet which is usually made from paper or plastic sheeting or film.

[0007] Additionally, on application of the laminate to a substrate, folds, wrinkles, and bubbles often appear. These are relatively difficult to remove because of the aggressiveness of the pressure sensitive coated sheet for the substrate. This can be particularly troublesome when the facing layer is relatively thin, such as, for example, a thin film of vinyl.

[0008] U.K. Patent Specification No. 1,541,311 published February 28, 1979 discloses a method of making a pressure sensitive adhesive coated laminate which overcomes many of the difficulties referred to above. The improvement therein disclosed involves the application between the pressure sensitive adhesive layer and the release surface of a means for decreasing the zero-minute peel value of the facing layer-pressure sensitive adhesive layer of the laminate. This means comprises a uniform and discontinuous layer of a coatable polysiloxane and, it is disclosed in said patent, that the presence of such means at the surface of the pressure sensitive adhesive yields a product which overcomes many of the disadvantages and handling difficulties present in products of this type previously available.

[0009] U.S. Patent No. 4,151,319 granted April 24, 1979, also discloses a method of making a pressure sensitive adhesive coated laminate which overcomes many of the difficulties referred to above. The improvement therein disclosed involves the application of a modified pressure sensitive adhesive layer containing a means for decreasing the zero-minute peel value of the facing layer-pressure sensitive adhesive layer of the laminate. This means comprises a material which produces a low zero-minute peel value intimately mixed in the pressure sensitive adhesive, e.g., a polysiloxane and, it is disclosed in said patent, that the presence of such means in the pressure sensitive adhesive yields a product which overcomes many of the disadvantages and handling difficulties present in products of this type previously available. Although the polysiloxanes used are eminently suitable, some of the newer more recently developed pressure sensitive adhesives, especially the water-based compositions, will be more advantageously used if improved means, especially siloxane compositions are provided, to secure such advantages, among others, such as lower face to face adhesion, better lubricity, and superior adhesion properties. Such improved pressure sensitive adhesive compositions and their use in preparing superior repositionable laminates are the subject matter of the present invention.

SUMMARY OF THE INVENTION

[0010] Applicant has discovered an improved method for the production of pressure sensitive adhesive coated laminates with superior properties wherein a first sheet having a release surface thereon is coated with a pressure sensitive adhesive to form a first laminate, and the first laminate is then subjected to conditions suitable to dry or cure the pressure sensitive adhesive, and the pressure sensitive adhesive side of the thus treated first laminate is married to the inner surface of a facing layer having inner and outer surfaces. The improvement involves the intimate mixing with the pressure sensitive adhesive prior to coating onto the release surface of a means for decreasing the "zero minute peel value" of the facing layer-pressure sensitive adhesive layer combination.

[0011] More particularly, by carefully selecting the material which is intimately mixed with the pressure sensitive adhesive a pressure sensitive adhesive coated laminate is obtained which is easily positioned and adhered to substrates and which can be removed, and, if necessary repositioned with ease during the application time. Specifically, the material used to decrease the "zero minute peel value" is an admixture of two polysiloxanes, hereinafter designated (i) and (ii), and the unique admixture must be capable of being intimately mixed and dispersed throughout the pressure sensitive adhesive composition, which can be water-based-, solvent-based-, solventless-, hot-melt-, and the like.

[0012] By virtue of the intimate mixing of the admixture of polysiloxane materials (i) and (ii) with the pressure sensitive adhesive, the need for a separate and precisely controlled coating step described in the above-mentioned U.K. Patent wherein the polysiloxane is applied to the pressure sensitive adhesive is obviated. The number of process steps required during actual assembly of the pressure sensitive adhesive laminate is thus decreased without any sacrifice in the utility of the end product obtained. Moreover, repositionability is enhanced over the simple mixtures of the above-mentioned U.S. Patent, because the siloxane component (i) appears to migrate to the air/adhesive interface placing a highly incompatible siloxane in the adhesive face while allowing the siloxane (ii) to remain partially soluble in the adhesive mass. Thus the admixed siloxanes (i) and (ii) act as a lubricant and result in a laminate with great improvement in terms of having a repositionable adhesive while maintaining adequate adhesion to the bonding substrate.

[0013] The product produced according to the method of the present invention after removal from the release surface, i.e., when it is about to be applied to the substrate, possesses a relatively low peel value, i.e., a low degree of affinity for the substrate. As a consequence, if, when applied to the substrate, the particular sheet is not straight or in the desired position, it is easily removed for repositioning. Moreover, if two areas of the pressure sensitive adhesive coated side of the sheet should touch one another, they are easily pulled apart without disturbing the uniformity of the coating of the pressure sensitive adhesive or stretching or wrinkling of the facing layer.

[0014] Furthermore, any air bubbles or wrinkles which occur in the laminate on application to the substrate, may be easily removed by smoothing with hand pressure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a schematic diagram of a process in accordance with the present invention; FIG. 2 is a drawing similar to FIG. 1 of another process in accordance with the present invention; FIG. 3 is a drawing similar to FIG. 1 of yet another process in accordance with the present invention; FIGS. 4, 5, 6 and 7 are sequential cross-sectional diagrams illustrating the formation of a laminate of the invention; and FIG. 8 is a graph showing improved repositionability provided by the new adhesive produced in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] Referring to the drawings, FIG. 1 shows a method for forming a laminate in accordance with the present invention comprising first coating a sheet of backing material 10, which suitably may be a kraft paper or other supportive sheet as defined hereinafter, from roll 12, which turns in the direction indicated by arrow A, with a suitable release material 14, such as, a silicone, or one of the other conventional materials used for this purpose.

[0017] The means for coating such material are well known, and as shown, a knife-coater 16 is utilized in the schematic. Thereafter, the coated sheet is passed through curing oven 18 which utilizes a conventional curing means, such as, heat, etc., to appropriately cure or set the release material. This produces a release surface 20 on release sheet 22. The release sheet 22 is coated with a modified pressure sensitive adhesive 24 using a knife-coater 26. The modification to the pressure sensitive adhesive involves incorporation of an admixture of polysiloxane (i) and polysiloxane (ii) into the adhesive in a manner which will be described in greater detail hereinafter.

[0018] Of course, various methods are known to the art for applying pressure sensitive adhesives and any of these conventional methods can be used to apply the modified pressure sensitive adhesive of the present invention. Typical methods in addition to knife-coating include, for example, spraying, roller coating and gravure roll coating.

[0019] In the embodiment of the invention shown in FIG. 1, pressure sensitive adhesive 11 from holding tank 13 and admixed polysiloxane (i) and polysiloxane (ii) 15 from holding tank 17 are metered into mixing vat 19 by metering valves

21 and 23, respectively. In the mixing vat, stirrer 25 intimately blends the pressure sensitive adhesive and the admixture of polysiloxanes (i) and (ii) which is subsequently delivered to the coating blade of knife-coater 26 through supply line 27 and valve 29.

[0020] As will be described in greater detail hereinafter, it is also possible to pre-mix the pressure sensitive adhesive and admixture of polysiloxanes (i) and (ii) at a place remote from the coating step of the present process and at a time prior to the coating.

[0021] After application of the modified pressure sensitive adhesive 24, the coated release sheet 22 is passed through oven 28 which utilizes conventional drying methods for pressure sensitive adhesive materials. Typically, temperatures in the range from 87°C to 138°C (190° to 280°F) for about 5 to 20 seconds are used. For pressure sensitive adhesives which are in a prepolymer form, a curing treatment is generally required. Such treatments are conventional in the art and may utilize heat and/or other means to effect curing.

[0022] Typically, the pressure sensitive adhesive layer 24 has a composition which will be as described hereinafter and generally has a thickness in the range from  $2.54 \cdot 10^{-3}$  mm to  $1.78 \cdot 10^{-1}$  mm (0.1 to 7 mils), and preferably from  $7.62 \cdot 10^{-3}$  mm to  $5.08 \cdot 10^{-2}$  mm (0.3 to 2 mils). Generally, it is coated in an amount, based on the dry solids weight, of from 0.3 to 8.0 mg./cm<sup>2</sup>.

[0023] Thereafter, the thus coated and cured sheet designated as 30 is married to an appropriate decorative or protective facing layer 32 unrolled from roll 34. The two layers are married by passing through nip rolls 36, 38 in a manner well known in the art. The pressure of nip rolls 36, 38 generally ranges from  $1.38 \cdot 10^4$  Pa -  $5.52 \cdot 10^5$  Pa (20-80 psi). Thereafter, the finished laminate is rolled onto roll 40 which revolves in the direction indicated by arrow B.

[0024] The overall thickness of the laminate is determined by the general end purpose for which it is to be used. Obviously, flexibility as well as weight would be factors which can be varied depending on this end purpose. Generally, however, in the sheet form of the present laminate intended for application by the consumer for general protective and decorating purposes the overall laminate thickness excluding the release layer is in the range from  $2.54 \cdot 10^{-2}$  mm to  $3.81 \cdot 10^{-1}$  mm (1 to 15 mils) and preferably is from  $7.62 \cdot 10^{-2}$  mm to  $1.27 \cdot 10^{-1}$  mm (3.0 to 5.0 mils).

[0025] The foregoing described process is generally referred to in the art as an indirect type coating process. That is to say, it is a process for forming the laminate of the present invention wherein the pressure sensitive adhesive material is coated onto the release layer first, and the thus coated release layer is subsequently married to the facing layer. When, either in use or in subsequent processing, the release layer is peeled from the facing layer, the pressure sensitive adhesive coating remains with the facing layer. Thus, the layer which is to remain with the facing layer is indirectly coated thereon by first coating it onto the release surface and then transferring the layer by virtue of the peeling step.

[0026] The other type of coating process conventionally used in the art is known as the direct type process. This process will be described in detail with reference to FIG. 3, hereinafter. However, generally, it refers to the process wherein the pressure sensitive adhesive layer is coated directly onto the inner surface of the facing layer and then the release layer is married to the thus coated facing layer. The ultimate product obtained, is, of course, the same in either case.

[0027] Referring now to FIG. 2, an indirect coating process is shown wherein the final laminate does not possess a separate release layer. Rather, the final laminate is generally in roll form and is composed of a facing layer which possesses an outer surface and an inner surface, the outer surface being a release surface. A substantially continuous layer of a pressure sensitive adhesive material is adjacent to and contiguous with the inner surface of the facing layer and also the outer release surface of the facing layer.

[0028] In use, it is thus necessary only to unwind the facing layer from the roll whereupon it is ready for use since there is no separate release layer to peel. This form is particularly useful when the laminate is in the form of narrow tape and the like.

[0029] Such a roll may be formed utilizing the process depicted in FIG. 2 wherein roll 42 which is a roll of backing sheet as described hereinabove having a release surface 44 is unwound in the direction shown by arrow C. The release surface 44 of the backing material is coated with admixed polysiloxanes (i) and (ii)-modified pressure sensitive adhesive 46 using coating knife 48 to form a laminate 50. The pressure sensitive adhesive 46, which has earlier been modified by the incorporation of the admixture of polysiloxanes (i) and (ii), is supplied to coating knife 48 from holding tank 45 through supply line 47 and valve 49.

[0030] The laminate 50 is then passed through drying or curing oven 52. Thereafter, the dried laminate 54 is married to facing layer 56 which is unwound from roll 58 in the direction indicated by arrow D. The marrying operation is carried out by passing the combination of layers 54 and 56 through nip rolls 60, 62 to produce married laminate 68.

[0031] It is noted that facing layer 56 possesses an inner surface 64 and an outer surface 66. The outer surface possesses release properties. That is to say, outer surface 66 has been treated in such a manner so as to possess or is composed of a material which inherently possesses good release properties relative to the pressure sensitive adhesive material used.

[0032] Thereafter, married laminate 68 is passed through separator rolls 70, 72 whereupon the release sheet 44 is

separated from the final laminate 74. At the separation point designated as E, the pressure sensitive adhesive layer remains with the inner surface 64 of facing layer 56 to form final laminate 74.

[0033] Release sheet 44 is wound onto roll 76 which may be reused. Final laminate 74 is wound onto roll 78 in a direction indicated by arrow F. Thus, by virtue of the winding operation, the final laminate 74 is rolled upon itself such that the adhesive coated surface 80 is immediately adjacent to and contiguous with the outer release surface 66 of the facing layer. As rolled, the laminate is now ready for cutting, packaging and use by the consumer or final user.

[0034] It is also noted that it is possible, in such an indirect coating process wherein the final laminate is produced in roll form without a separate release layer, for release sheet 44 to be disposed in the form of an endless belt which would avoid rewinding it onto roll 76.

[0035] FIG. 3 illustrates yet another method by which the laminate of the present invention can be produced in roll form without the presence of a separate release sheet in the final roll. Particularly, FIG. 3 shows the direct method of coating referred to hereinabove. In this method, roll 82 of a facing layer having an outer surface 84 which possesses release properties and an inner surface 86 is unwound from roll 82 in the direction indicated by arrow G. The inner surface of facing layer 86 is coated with admixed polysiloxanes (i) and (ii)-modified pressure sensitive adhesive material 88 using knife coater 90 to form a laminate 92. The laminate 92 is passed through drying oven 94 and the dried laminate 96 is rolled upon itself into roll 98 by winding in the direction indicated by arrow H. By virtue of winding in this direction, it is clear that the inner surface 86 of the facing layer which has thereon the coating of pressure sensitive adhesive is rolled such that the adhesive is adjacent to the outer release surface 84 of the laminate.

[0036] It is further clear that the process depicted in FIG. 3 could be carried out such that subsequent to exiting oven 94, laminate 96 may be married to a separate release sheet in the manner shown in FIG. 1 to form a final product having a separate release sheet.

[0037] In the case when the final product does not have a separate release sheet, it is possible to place it in stack form rather than in the form of a roll. Thus, referring to FIG. 3, after exiting oven 94, the laminate 96 may be cut into separate and equally sized pieces or sheets and the separate sheets can be stacked one upon the other such that the pressure sensitive adhesive layer of one sheet is immediately adjacent or next to the release surface of the facing layer of the next sheet in the stack. In use, therefore, it is only necessary to peel off the top sheet whereupon the next, uncovered sheet, presents itself for further use.

[0038] In the following discussion, reference will be made only to that embodiment of the present laminate wherein a separate release layer is present. It is clear, however, that the discussion also is applicable in all respects to those embodiments of the present laminate wherein a separate release layer is not present.

[0039] Referring now to the figures which depict a laminate in accordance with the present invention, FIG. 4 shows a conventional backing layer 100 used for a pressure sensitive adhesive laminate. This material is generally referred to as a release sheet, although, in actuality, it may be fabricated from two separate components, namely a supporting sheet, such as, kraft paper or other material having sufficient dimensional stability to act as a supporting sheet, and a coating of a release material thereon as described hereinabove. Such sheets may also be impregnated with the release material.

[0040] The most well known and economical type release sheet used presently is an unbleached kraft paper directly coated on one or both sides with a cured silicone. It is possible however, to use other release materials, such as, glassine papers, spun bonded synthetic non-wovens, e.g., polyethylene, or continuous films of extruded synthetics, e.g., polyesters, polyethylene, polypropylene, cellophane, and the like, which possess release properties in the untreated state. Generally, however, the inherent release properties of such films are not sufficient and must be improved by coating with release compositions, such as, the cured silicones mentioned hereinabove.

[0041] Such release sheets or surfaces, and methods for their preparation are well known. Typically, the paper or backing sheet is dipped into a bath of a silicone release agent, or coated on one or both sides with the release agent, and then cured. Such methods are described in U.S. Pat. No. 3,503,782. Alternately, the release material may be knife or roller coated onto a sheet.

[0042] In any event, regardless what type release material is used, it is necessary only that the release surface 102 of the supporting or backing sheet 100 possess properties of good release with respect to pressure sensitive adhesive materials.

[0043] Alternately, the release surface can be the outer surface of the facing layer of the laminate such that the laminate is rolled upon itself as described hereinabove with reference to FIGS. 2 and 3. The release properties may be an inherent quality of the outer surface of the facing layer or a quality imparted through conventionally known finishing or coating techniques.

[0044] Referring now to FIG. 5, a layer of a modified pressure sensitive adhesive material 104 is coated on top of the backing sheet of FIG. 4 to form a laminate sometimes referred to hereinafter as a "first laminate". As stated hereinabove, the pressure sensitive adhesive has been modified by incorporation of an admixture of polysiloxanes (i) and (ii) therein and the coating of the modified pressure sensitive adhesive layer 104 may be accomplished by conventional methods, e.g., knife-coating, spraying, roller coating and gravure roll.

[0045] The pressure sensitive adhesive 104 may be one from a well known class of adhesive materials generally available in the art modified in the manner which will be described hereinafter. Typically, such a conventional adhesive comprises a two component system, one component of which is a polymer or resin which is intrinsically tacky, such as, a tacky elastomer, or has intermixed therewith, a resin imparting tackiness and a second component which is a tack controlling component to reduce the tack of the adhesive layer to the desired peel bond value. The second component also imparts cutting properties to the adhesive layer so that it will cut when the transferrable film, i.e., the facing layer is cut.

[0046] Also, as shown in FIG. 7, it is important in the use of conventional pressure sensitive adhesive materials that the adhesive layer, 104, remain with the facing layer, and not with the release layer 100 upon stripping.

[0047] The second component is preferably a readily deformable material in order to allow the adhesive layer to make adequate contact with the receiving surface of the substrate which may be rough in texture. The tack controlling component is usually present in concentrations of from about 6 to 65 parts per 100 parts of the total tacky compound. Intrinsically tacky polymers include polyacrylic or methacrylic esters and acids; polyvinyl ethers; co-polymers of vinyl ethers and the aforesaid acrylic compounds; polyisobutylene and polybutenes; natural rubber; synthetic polyisoprene; polyvinylesters; polychloroprene; polybutadiene and co-polymers of butadiene with styrene.

[0048] Tackifying resins include hydrocarbon resins, terpene resins, such as, polybeta-pinene resin; resin derivatives, such as, hydrogenated resins and esters and liquid mixtures of polymeric styrene and homologues. Preferred materials are polyvinylbutylether; polyvinylethylether; polyvinylmethylether; polybutylacrylate or co-polymers of butylacrylate and methacrylate. Special mention is made of polyacrylates, and especially poly(n-butyl acrylate), poly(2-ethylhexyl acrylate), mixtures thereof, and the like).

[0049] A detailed description of such materials is set forth in U.S. Pat. No. 2,432,376.

[0050] Subsequent to the application of pressure sensitive adhesive layer 104, the laminate is subjected to a drying or curing step, such as, for example, heating, and other methods which are conventionally used for such pressure sensitive adhesive materials. Understandably, the particular method used will be dependent upon the nature of the pressure sensitive adhesive material used; however, such methods are conventional in the art.

[0051] The pressure sensitive adhesive materials conventionally used are either soluble or dispersible in water or organic solvents. Also, materials have been developed which are themselves liquids, or possess relatively high solids content, but nevertheless can be coated or applied without dilution or emulsification. Also known are materials known as the "hot melt" type which are rendered coatable by heating. However, the particular type of pressure sensitive material used is not critical so long as it fulfills its function as a pressure sensitive adhesive and does not adversely affect the other desirable properties of the laminate.

[0052] Subsequent to the curing step, a facing layer 106 is married to the first laminate of FIG. 5 to form the final laminate shown in FIG. 6.

[0053] Facing layer 106 is generally a sheet-like material which can be decorative or protective in nature and can be wood, including wood veneer, metal, such as, metal foil, paper or a plastic film forming material, e.g., vinyl polymers such as, polyvinyl chloride, polyvinylidene chloride, copolymers of polyvinyl chloride and polyvinylidene chloride; polyolefins, e.g., polypropylene, polyethylene; polyesters, and woven or non-woven fabric. Typically, the facing layer may have a decorative pattern embossed, printed, or otherwise imposed thereon. Alternately, the facing layer may be composed of two or more separate sub-layers.

[0054] For example, it is possible to use a top layer which is a substantially transparent sheet of a protective film, e.g., polyvinyl chloride, polyvinylidene chloride, copolymers of polyvinyl chloride and polyvinylidene chloride; polyester, polypropylene, polyethylene, polyacrylate, urethanes, hard surfaced resins, etc., and a lower sheet which may be composed of the same type materials as described hereinabove with respect to a single facing layer.

[0055] Generally, such a transparent layer can serve the function both of protecting the decorative pattern of the bottom facing sheet, and in addition, can itself contribute to the over-all decorative appearance of the laminate, as by producing a shiny effect or high gloss.

[0056] Other types of decorative facing layers, such as, flocked fabrics or films, and polymeric films, such as, polyester films having a thin deposit of metal thereon (metalized), vinyl films coated with resin-pigment combinations in a decorative pattern, and the like can be used as the facing layer.

[0057] FIG. 7 shows the method of utilization of the laminate in accordance with the present invention wherein components 104 and 106, generally designated as 108, are separated from backing sheet 100.

[0058] After stripping backing layer 100 from layers 108, the combination of layers designated 108 may be applied to the desired substrate, e.g., furniture, walls, cabinet surfaces, etc. By virtue of the unique properties of laminate 108 bestowed on it by the modification of the pressure sensitive adhesive which will be described hereinafter, it is possible to easily position layer 108 onto the substrate, to easily remove it and to reposition it if necessary. Moreover, if portions of the pressure sensitive adhesive side of laminate 108 should touch one another, they are easily pulled apart without disturbing the uniformity of the pressure sensitive adhesive layer. Consequently, the usual tangles, wrinkles, creases, stretches, etc., frequently encountered with pressure sensitive coated material of this type are avoided.

[0059] From the above it can be seen that the laminate of the present invention possesses a number of advantageous properties as compared to the majority of laminates generally used for the same type of purpose which have been previously known. The disadvantages of such prior laminates have been outlined hereinabove. More particularly, by virtue of the nature of the modification of the pressure sensitive adhesive used in the laminate of the present invention the present laminate, over all, is substantially easier to handle with respect to its application to a substrate than are most prior known laminates.

[0060] Thus, generally, the present laminate (after separation of the release layer), upon being initially positioned onto the desired substrate, for example, a wall, can be easily removed without any adverse affects should it be desired to reposition the laminate. This might occur, for example, in the case where the laminate, in its initial application to the substrate, was not straight, or possessed wrinkles, or bubbles. In such a case, the laminate may be easily removed by the applier without stretching the laminate or difficulty in pulling it from the substrate.

[0061] Moreover, should the laminate, during application, become folded upon itself so that different areas of the pressure sensitive adhesive surface touch one another, they, in turn can be easily pulled apart without difficulty by the applier, and without adversely affecting the laminate for purposes of its reapplication.

[0062] Additionally, once the laminate has been applied to the satisfaction of the applier, it possesses sufficient adhesion to the substrate, so as to remain in the position applied. Also, over a period of time, for example, 20 minutes to an hour, the adhesion, or peel value as it is hereinafter defined, increases to a sufficiently high value to produce a permanent application to the substrate.

[0063] It is difficult to quantify the ease or difficulty with which the laminate can be initially applied or after such initial application, removed from the substrate. Thus, the ease of application of the laminate depends on the skill of the person applying the laminate as well as the nature of the particular substrate to which it is being applied. Many types of substrates, for example, walls, composed of painted wall board, painted cinder block or plastic, etc., will be encountered by the typical user of this laminate, i.e., the consumer. As a result, depending on the particular nature of the end use, the ease of application and specific properties with respect to degree of adherence encountered with each of the different types of substrates will vary in an undeterminable manner.

[0064] Unquestionably, however, for any given substrate, the person using the present laminate will encounter substantially less difficulty in applying the laminate of the present invention as compared to use of the majority of prior art laminates, i.e., a laminate without the specific modification to the pressure sensitive adhesive required in the present invention or that described in previously mentioned U.K. Patent Specification No. 1,541,311 and U.S. Patent No. 4,151,319.

[0065] Specifically, the pressure sensitive adhesive layer of the laminate of the present invention possesses means for decreasing the "zero minute peel value" (as defined hereinafter) of the facing layer-pressure sensitive adhesive layer combination composed of an admixture of polysiloxanes (i) and (ii) intimately mixed with the pressure sensitive adhesive prior to the adhesive layer being coated.

[0066] Thus, by virtue of the presence of the polysiloxane admixed components of the present laminate, there is produced a substantially decreased initial adhesion of the laminate for a particular substrate as compared to that which would be encountered with a laminate not possessing the mixed polysiloxanes (i) and (ii) component.

[0067] Additionally, however, the amount of actual adhesion at the time of initial application of the laminate to the substrate is sufficiently improved, even with respect to that of U.S. Patent No. 4,151,319, so as to assure that the laminate will remain adhered to the substrate and not separate by virtue of the laminate's own weight.

[0068] Moreover, as noted hereinabove, the adhesion of the laminate of the present invention to the substrate builds up within a reasonable amount of time so as to provide a permanent installation which is essentially equivalent to that obtained with a laminate without the improvement of the present invention, and superior to that achieved with the technology disclosed in U.S. 4,151,319.

[0069] Yet a further advantage of the present invention is its unusual characteristic of regenerating relatively low zero minute peel values after a substantial residence time on a substrate. That is to say, if the present laminate is applied to a given substrate and allowed to remain for a given period of time, e.g., eight hours, upon removal from the substrate (assuming such removal can be effected without mutilating or destroying the substrate or laminate), it has been found that the laminate will exhibit a relatively low zero minute peel value. Thus, the unique properties of the present laminate with respect to its ease of initial application are not destroyed by virtue of such application, but continue to reappear should it be necessary to remove the laminate from the given substrate.

[0070] Another important feature of the laminate of the present invention is its superior slip characteristics relative to the substrate, even in comparison with those produced following the teachings of U.S. Patent 4,151,319. While this characteristic depends to some extent on the substrate involved, invariably, the lateral slip is substantially better with the present laminate than with a Control Laminate (defined hereinafter), or with one prepared using either polysiloxane (i) or polysiloxane (ii), alone, to modify the pressure sensitive adhesive. As used herein, the term "slip" means the ability of the laminate to slide on the substrate under light hand pressure. This property is quite difficult to quantify, although it is quite noticeable to the applier, and depends on the "lubricity" of the modified pressure sensitive adhesive.



[0071] In order to more quantitatively characterize the improved properties of the present laminate, the discussion following hereinafter will utilize a number of defined terms relating to the degree of adhesion of the laminate to a given substrate after a specified amount of time. Additionally, because, as noted above, many different types of substrates will be encountered, in an attempt to generally characterize the substrates, the defined values will be further limited to specific test substrate materials which are also described in detail hereinafter.

[0072] Additionally, in characterizing the properties of the present laminate, it is necessary to define such characteristics in terms of the difference between those same characteristics possessed by a Control Laminate. Such a Control Laminate consists of a laminate which is identical to the laminate of the present invention, except for the fact that the pressure sensitive adhesive does not contain the polysiloxane of the present invention.

[0073] Referring now to the polysiloxane utilized to modify the pressure sensitive adhesive, it must be devoid of certain properties which, if possessed, would make it unsuitable for use in the present laminate. That is to say, if it possessed such properties, the resulting laminate would not possess the advantages of the present laminate. For example, the polysiloxane material should preferably possess some affinity for the pressure sensitive adhesive.

[0074] In this respect, the polysiloxane utilized in the present invention may be qualitatively characterized as a non-release material. That is to say, in the art, a "release material" is generally considered to be one which possesses relatively low affinity for a pressure sensitive adhesive and which easily separates from the pressure sensitive adhesive on peeling.

[0075] Thus, a substantial portion of the polysiloxane component of the pressure sensitive adhesive which may be at or near the interface of the pressure sensitive adhesive layer and the release surface will preferentially remain with the pressure sensitive adhesive layer rather than the release surface when the release surface is stripped from the pressure sensitive adhesive layer. Consequently, in this context, the polysiloxane possesses "non-release" properties.

[0076] In a similar manner, the polysiloxane material must possess certain other properties in order to make it suitable for use in the present laminate. Thus, the polysiloxane material must be dispersible or must have the capacity to be rendered dispersible through conventional chemical or mechanical means, e.g., viscosity modification, forming a solution of the polysiloxane in an appropriate solvent, heating, milling etc.

[0077] In addition, the dispersion of an effective amount of the polysiloxane material throughout the pressure sensitive adhesive layer should not cause a substantial decrease in the adherence of the pressure sensitive adhesive for the facing layer. Further, the polysiloxane material should not substantially adversely affect the ability of the pressure sensitive adhesive to achieve a strong but removable adherence of the laminate to the substrate to which it is applied. As used herein, the term "intimately mixed", "completely dispersed" and the equivalent are meant to imply that the polysiloxane material is uniformly distributed throughout the pressure sensitive adhesive. It is believed that the polysiloxane material is present in the pressure sensitive adhesive in the form of a multiplicity of small beads or droplets. However, it is apparent, that the polysiloxane material cannot be uniformly distributed in the form of relatively large globules, which, while large, are spaced equal distances apart in the pressure sensitive adhesive. Thus, a typical distribution of the polysiloxane material in the pressure sensitive adhesive would have a multiplicity of such small droplets or beads within each square inch of the pressure sensitive adhesive layer of the laminate. FIGS. 5, 6, and 7 of the drawings illustrate this type of structure.

[0078] More specifically, the polysiloxane component (i) should have only slight or ideally no solubility into the organic pressure sensitive adhesive as well as any water carrier which may be present. On the other hand, the organopolysiloxane component (ii) should be readily soluble in water as well as being soluble in the polysiloxane (i). Upon removal of water from the pressure sensitive adhesive, polysiloxane (i) is prone to separate from the adhesive and bloom to the surface carrying with it some of the water soluble organopolysiloxane (ii). Polysiloxane (i) which has migrated to the adhesive/air interface is a more efficient lubricant for the manufacture of a repositionable adhesive when compared to the more adhesive soluble organo silicone (ii). The resulting advantages are manifested as follows:

- 1) Less silicone is required to give superior results with regards to repositioning the adhesive.
- 2) Less silicone is intermixed with the adhesive mass and therefore better cohesive and adhesive properties can be maintained.
- 3) The polysiloxane (i) having lower surface tension than the more organic liking silicone (ii) permit superior repositionability of the adhesive while having faster wet-out of the adhesive to the bonding substrates and, therefore, superior adhesion to the same substrates.

[0079] It is to be understood, of course, that many other configurations of the polysiloxane admixture within the pressure sensitive adhesive layer are possible wherein droplet size and placement are modified. The skilled artisan would be aware, after an understanding of the present invention, of various configurations which may be desirable to produce a laminate possessing an appropriate zero minute peel value for any particular end use.

[0080] It is apparent that the distribution of the polysiloxane admixture can be effected in a variety of ways. However, the most preferred method of distribution has been found to be that obtained through a low speed, low shear mixing

for at least several hours.

[0081] The speed and shear are preferably sufficiently low to prevent substantial quantities of air from being introduced into the pressure sensitive adhesive. The introduction of large quantities of air and resultant foaming of the adhesive can retard formation of the required intimate mixture of the polysiloxane admixture in the adhesive or can result in uneven coating of the adhesive.

[0082] The time and speed of mixing are dependent upon the batch size and physical properties of the polysiloxane admixture and the pressure sensitive adhesive. For large commercial batches, for example, 15100 l - 18900 l (4,000-5,000 gallons), mixing times of 6 to 20 hours and preferably 14 to 16 hours at mixing speeds, with a two-blade stirrer, of 30 to 200 revolutions per minute and preferably 60 to 65 revolutions per minute have generally yielded acceptable mixtures. For smaller drum size batches, typically 208 l (55 gallons), mixing with a two blade stirrer for 1 to 3 hours and preferably about 2 hours at 30 to 200 and preferably 60 to 65 revolutions per minute has been found acceptable.

[0083] Acceptable mixing conditions can easily be determined by the skilled art worker since it is necessary only that an intimate and uniform mixture be obtained. Generally, the higher the speed of mixing, the less time required, and the larger the batch size, the greater the time required.

[0084] The polysiloxane admixture must, therefore, be in a physical form suitable for allowing it to be intimately mixed or dispersed throughout the pressure sensitive adhesive material without adversely affecting the suitability of the adhesive for use in such a laminate.

[0085] Consequently, the property of being dispersible, as that term is used herein, does not necessarily mean, that the polysiloxane admixture, in and of itself, must be of such a viscosity (or molecular weight), that it can be dispersed without further dilution or emulsification. It is sufficient that the material be susceptible to such dilution or emulsification, or other treatment, so as to allow it to be dispersed uniformly throughout the pressure sensitive adhesive. Typically, for example, such material can be formed into an emulsion (generally an aqueous emulsion) or dissolved in an appropriate solvent.

[0086] Understandably, the molecular weight, or the viscosity of the polysiloxane components (i) and (ii) is a factor in determining whether or not the material will be dispersible in accordance with the above definition. Considering the nature of the specific polysiloxane materials defined hereinbelow, it is clearly within the skill of the art worker to adjust the molecular weight, and/or the viscosity of the material so that it is dispersible. Tests have shown that a range of molecular weights and/or viscosities of polysiloxane (i) are useful in the processes of the invention. It has been observed the higher viscosity or higher molecular weight siloxanes (i), however, appear to give the best results in terms of repositionability. However, the lower viscosity polysiloxanes (i) appear to give a slightly higher adhesion value. The best range for the lubricant application appears to be in the range of 1 to 3 Pa-s (1,000 to 3,000 cps). prior to addition to the pressure sensitive adhesive. Furthermore, it has also been observed that as the viscosity of the silicone increases, the more difficult it is to mix into the adhesive and maintain a continuous film when coated onto a supporting substrate.

[0087] It has been found advantageous, due to the small quantity of polysiloxane admixture used relative to the amount of adhesive, to initially pre-mix the polysiloxane in a suitable solvent prior to incorporation into the adhesive. For example, when a water soluble polysiloxane and water based adhesive are used, it is desirable to pre-mix the polysiloxane admixture in water prior to incorporation into the adhesive. Similarly, if an organic solvent system is being used, it is desirable to pre-mix the polysiloxane admixture in a suitable organic solvent, e.g., isopropyl alcohol, prior to incorporation into the adhesive. Generally, a mixture of polysiloxane to solvent of from about 1:2 to 1:5 is helpful in obtaining the fastest final mixture of polysiloxane in adhesive. Of course, any water or other solvent added as part of the pre-mix must be taken into account in computing the final solids content and viscosity of the resulting modified pressure sensitive adhesive.

[0088] With respect to the characterizing parameters used herein, the following constitute defined terms:

#### 1. PEEL VALUE

[0089] Die-cut 2.54 cm x 15.24 cm (1" x 6") samples of the laminate are mounted on 5.08 cm x 15.24 cm (2" x 6") surfaces of "Stainless Steel", "SBR" or "Acrylic" surfaces, as defined hereinafter. The specimens of the laminate are mounted by first removing the backing release sheet and placing the adhesive coated component in the center of the test panel. The specimen is smoothed onto the panel lightly with the hand leaving the last inch of the specimen free from the panel. Thereafter, a strip of the backing paper that was removed is placed under the last free inch in order to provide means for lifting the specimen from the test panel.

[0090] The specimen is then rolled using a 2 kg (4 1/2 pound) rubber hand roller for 15 seconds in each direction employing no additional hand pressure, i.e., the total pressure is supplied by the weight of the roll itself.

[0091] The sample is then allowed to remain at room temperature for the specified period of time. In the case of the "zero minute peel" value or peel value at zero time, the specimen is removed from the panel with 10-15 seconds actual elapsed time from the time of mounting.

## EP 0 619 352 B1

[0092] The test panel is mounted into the lower jaw of an Instron machine Model No. TM-2360-011, and the free end of the strip of backing paper is placed in the upper jaw. The sample is then peeled back on itself at an angle of 180° for a distance of 6.35 cm (2.5 inches) and the average peel adhesion strength is recorded in grams per inch of width. This value represents the peel value for the indicated time period.

### 2. STAINLESS STEEL SURFACE

[0093] The stainless steel surface is a sample of stainless steel conforming to QQ-S-766, Class 302 or 304 (AISI 302 or 304) stainless steel having a bright annealed finish. The surface roughness height is  $5.08 \times 10^{-6} \text{ cm} \pm 2.54 \times 10^{-6} \text{ cm}$  (2.0 micro inches  $\pm$  1.0 micro inches) arithmetical average deviation from the mean line, as obtained from the Pressure Sensitive Tape Council, 1201 Waukegan Road, Glenview, Illinois 60025.

### 3. "ACRYLIC" SURFACE

[0094] A 0.95 cm (3/8") standard wallboard surface painted with two coats (with a roller) of an interior white acrylic based latex paint (DuPont Lucite 2360 interior latex paint).

### 4. "SBR" SURFACE

[0095] A 0.95 cm (3/8") standard wallboard surface painted with two coats (with a roller) of styrene-butadiene rubber based paint (Sherwin Williams Latex Interior Edgewater Blue).

### 5. FACE-TO-FACE PEEL VALUE

[0096] Two die-cut 2.54 cm x 15.24 cm (1" x 6") samples of the laminate with the release sheet removed are married adhesive coated side to adhesive coated side and are rolled using a 2 kg (4 1/2 pound) rubber hand roller for 15 seconds in each direction employing no additional hand pressure, i.e., the total pressure is supplied by the weight of the roll itself. The last inch of each sample is unbonded in order to provide means for separating the samples from one another. This is accomplished by inserting a small piece of release sheet between the samples at this point.

[0097] Immediately following rolling, the test samples are mounted into the jaws of an Instron machine Model No. TM-2360-011, and the samples are then peeled apart at an angle of 180° for a distance of 6.35 cm (2.5 inches) and the average peel adhesion strength is recorded in grams per 2.54 cm (inch) of width.

### 6. RELEASE VALUE

[0098] A die-cut 2.54 cm x 15.24 cm (1" x 6") sample of the laminate with the release sheet attached is tested for the force required to separate the release sheet from the adhesive coated facing sheet.

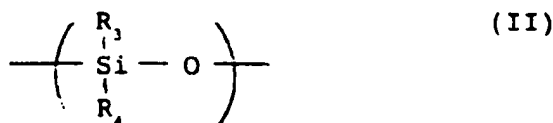
[0099] One inch of the release sheet is peeled back by hand and is mounted into the jaw on an Instron machine. The release sheet is mounted into the upper jaw and the adhesive coated facing layer is mounted into the lower jaw. The release sheet is then peeled from the facing layer at an angle of 90° for a distance of 6.35 cm (2.5 inches) and the average peel adhesion strength, indicating release value, is recorded in grams per 2.54 cm (inch) of width. Unless otherwise specified, all viscosities were measured at 25°C (room temperature) using a Brookfield Synchro-Lectric, Model LVT viscometer and are reported in Pa-s and centipoises (cps).

[0100] Referring now in greater detail to the polysiloxane materials, those materials that have been found to possess all of the above noted properties, and to produce the superior advantageous properties in the presently claimed laminate are an admixture of polysiloxanes (i) and (ii),

said polysiloxane (i) being substantially water-insoluble and insoluble in said pressure sensitive adhesive and formed from monomeric units having structures (I) and (II) as follows:



and

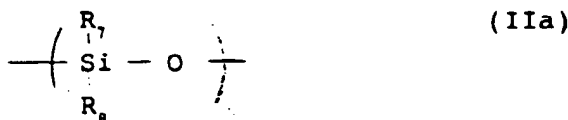


wherein  $R_1$  is methyl, ethyl, phenyl, tolyl, or a mixture of any of them,  $R_2$  is methyl, ethyl or phenyl; and  $R_3$  and  $R_4$  are the same or different and are methyl or ethyl, wherein the majority of units (I) and (II) comprise units (II), and said polysiloxane (i) has a viscosity in the range of from 0.005 to 60 Pa-s (5 cps to 60,000 cps) measured at 25° C with a #4 spindle at 30 rpm; and

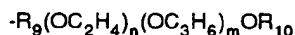
said polysiloxane (ii) being water-soluble and compatible with polysiloxane (i) and formed from monomeric units having structures (Ia) and (IIa) as follows:



and



wherein  $R_5$  is a polyoxyalkylene group having the structural formula



wherein  $R_{10}$  is hydrogen or a monovalent hydrocarbon group having from 1 to 10 carbon atoms and  $R_9$  contains both oxyethylene and oxypropylene units,  $R_6$  is an alkylene group having at least two carbon atoms,  $n$  and  $m$  are numbers, the sum of  $n$  and  $m$  is at least 1 and the oxyalkylene unit  $R_{10}(\text{OC}_3\text{H}_6)_m(\text{OC}_2\text{H}_4)_n$  has a molecular weight of at least 80, and wherein there are at least two units having structure (Ia) and at least three units having structure (IIa) and wherein the oxyalkylene unit constitutes from 85 to 30 weight percent of the polysiloxane polymer;  $R_6$  may be methyl, ethyl, or phenyl; and  $R_7$  and  $R_8$  may be the same or different and may be methyl or ethyl, and said polysiloxane (ii) has a viscosity in the range of from 0.05 to 5 Pa-s (50 to 5000 cps) measured at 25° C with a #4 spindle at 30 rpm, the amount of polysiloxane (i) in said admixture being effective to separate from the adhesive and to bloom to the adhesive/air interface of an article coated with said adhesive composition to provide efficient repositionability and the amount of polysiloxane (ii) in said admixture being effective to provide faster wet-out of the adhesive to a bonding substrate and, ultimately, superior adhesion thereto.

**[0101]** A preferred class of polysiloxanes used as component (ii) (Ia) are those described in U.S. Pat. No. 3,505,377 and U.S. Pat. No. Re. 27,541.

**[0102]** Particularly preferred in this class is a hydrolytically stable silicone surfactant composition containing a dimethylsiloxane-oxyalkylene block copolymer wherein the oxyalkylene unit of the copolymer contains oxyethylene and oxypropylene units.

**[0103]** These compounds preferably possess a molecular weight of at least 1500 and in the structural formula,  $R_6$  is a monovalent hydrocarbon group having from 1 to 10 carbon atoms. Generally, the oxyalkylene unit comprises 15 to 60 weight percent oxyethylene units and there are at least about three units having structure (Ia) and at least about 40 units having structure (IIa).

**[0104]** Most preferably in this embodiment,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_6$ ,  $R_7$  and  $R_8$  are methyl and the polysiloxane possesses a viscosity at room temperature of 2 to 2.6 Pa-s (2000 to 2600 cps.) as measured with a #4 spindle at 30 rpm.

**[0105]** Another preferred class of polysiloxanes wherein  $R_5$  is the polyoxyalkylene group described hereinabove are

those wherein  $R_{10}$  is hydrogen. This means that the polyoxyalkylene unit is capped with a hydroxyl group at its terminus (herein referred to as hydroxy capped). Generally, the oxyalkylene unit is composed of oxyethylene and/or oxypropylene segments and it possesses a molecular weight in the range from 80 to 660. The weight percent of the OH groups is preferably in the range from 0.9 to 4.5. These materials exhibit viscosities in the range from 40 to 45 centistokes.

[0106] In all cases wherein an oxyalkylene group is connected to a silicon atom in the main siloxane chain, it is attached through a non-hydrolyzable carbon-silicon bond.

[0107] It is noted that the above polysiloxanes can be referred to as either graft or block polymers, depending on the specific structure of the polymer and/or on the manner in which they are synthesized.

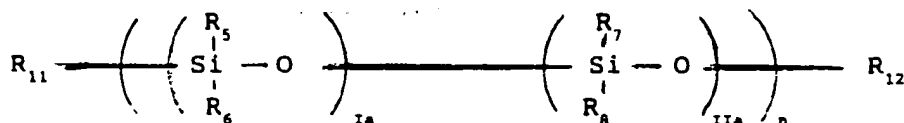
[0108] It is noted that inasmuch as the siloxane polymers utilized as the adhesive modifiers in the present laminate, must be dispersible, they are, generally, not cross-linked, nor do they cross-link over a period of time under normal storage conditions or in the absence of crosslinking agents.

[0109] The primary lubricant (i) is based on polysiloxanes having a viscosity range from 0.005 to 60 Pa.s (5 cps to 60,000 cps) and a monomeric structure unit composed mainly of polydimethyl siloxane units. The primary lubricant can also have another monomeric structure unit attached to the dimethylpolysiloxane chain. It is only critical however that the majority of any such copolymer be based on the dimethylpolysiloxane. Examples of copolymers that will also work are numerous, i.e., such as phenyl methyl dimethyl polysiloxane. The best lubricants will always be based on the majority of the polymer or copolymer (i) being dimethylpolysiloxane.

[0110] As used herein, the term "prime mole percent" is the number ratio of the x type to y type siloxane units.

[0111] Such polysiloxanes as well as methods for their production are conventional and are described in detail in U. S. Pat. No. 2,560,498.

[0112] Typically, the polysiloxanes which can be used in the present invention have the structural formulae:



wherein  $R_1 - R_8$ , inclusive, and the prime mole percent or number of structural units designated I, Ia, II and IIa are as defined above.  $R_{11}$  and  $R_{12}$  are polymer chain terminal groups. In the case of relatively long length polymer chains, i.e., high molecular weight polymers, the particular groups constituting  $R_{11}$  and  $R_{12}$  are present in trace amounts. Consequently, the effect of such groups, even if they are chemically reactive, i.e., can react with certain of the other chemical entities in the polymer, is minimal, and, as a practical matter, undetectable. In such a case, while it is preferred that  $R_{11}$  and  $R_{12}$  are hydrogen or saturated lower alkyl, e.g., having 1 to 10 carbon atoms, the particular chemical nature of such terminal groups is not critical so long, of course, as the groups do not adversely affect the desired properties of the polysiloxane.

[0113] In the event that the polymer chain is of shorter length, i.e., lower molecular weight, the terminal groups will, of course, provide a correspondingly greater contribution to the overall chemical and physical properties of the polymer. This is due to the increased proportion of the overall molecular weight represented by the terminal groups. Thus, in the relatively low molecular weight polysiloxanes used in the present invention, e.g., those possessing hydroxy capped oxyalkylene units, the hydroxyl groups do play a role in the overall properties of the polymers.

[0114] The subscript "n" represents the molecular weight of the polymer and, as discussed hereinabove, is such that the respective polysiloxanes are dispersible.

[0115] As stated hereinabove the polysiloxane admixtures utilized in preparing the laminate of the present invention may be mixed or dispersed into the pressure sensitive adhesive using a variety of techniques well known and conventional in the art. Thus, for example, the polysiloxane whether it is used as is, or diluted either in a solvent or an aqueous emulsion may be blended into the pressure sensitive adhesive after manufacture of the adhesive, but prior to packaging; or at the plant where the adhesive is to be used, either by mixing the polysiloxane admixture into batches of adhesive or metering and dispersing the polysiloxane admixture into the adhesive immediately prior to the coating step during

fabrication of the laminate. It is thus within the skill of the art to use any of these methods to introduce the polysiloxane material and to regulate the parameters affecting the distribution, e.g., mixing speed, configuration of mixing blades, duration of mixing, etc., so as to produce a uniform dispersion.

[0116] Insofar as the actual physical form of the polysiloxane admixture with respect to the dispersing technique is concerned, any type of conventional organic solvent e.g., aliphatic and aromatic organic solvents can be used. The controlling factor in the selection of such a solvent is merely that it be one which is commercially available and does not have an adverse influence on either the economics of the process or product and of course, does not adversely affect the product itself.

[0117] Alternately, the polysiloxane admixtures may be incorporated into an aqueous emulsion using conventionally known emulsifying agents and conventional emulsifying techniques. Here again, such techniques are well known to the skilled artisan in this technical field.

[0118] It is further possible, depending on the viscosity of the undiluted polysiloxane admixture, to use it as is, without a diluent. The amount of polysiloxane admixture used can vary over a wide range and depends on the specific polysiloxanes which are used, the technique used for dispersing the polysiloxanes, the nature of the specific adhesion properties or tack properties of the pressure sensitive adhesive, and other parameters which would be characteristic of the specific process being used. However, conventional art techniques could be used to adjust and to optimize these parameters in order to optimize the product properties.

[0119] It has been found, generally, that a concentration of the admixed polysiloxanes of from 0.001 to 20% by weight, and most preferably from 0.1 to 1.0% by weight, based on the solids content of the pressure sensitive adhesive will lead to a product having properties within an optimal range.

[0120] In any event, the specific amount of polysiloxane admixture and the specific manner of its dispersion should be regulated so as to produce a substantial decrease in the zero minute peel value of the product as compared to a control laminate and to provide for a twenty minute peel value of at least about 100 grams. Preferably, the reduction in the zero minute peel value as compared to the zero minute peel value of the control laminate is in the range of at least greater than about 25%. It is possible of course, that for a specific purpose, the skilled artisan might desire to decrease the percent reduction in the zero minute peel as compared to the control laminate.

#### DESCRIPTION OF ADDITIONAL PREFERRED EMBODIMENTS

[0121] The following examples illustrate the present invention:

##### EXAMPLE 1

[0122] A release sheet is prepared from kraft paper (42 pounds per ream) by coating it with a conventional silicone release finish, for example, Dow Corning Syloff 23 with DC 23A catalyst, the amount of coating being about 0.23 kg (0.5 pounds) per ream. The paper is coated on the machine finished side. The coating is carried out using an 80 line quadrangular gravure coating roll.

[0123] The solids content of the silicone release material in Tulusol 50 (a 1:1 mix of toluene and heptane) is 3.8%. After coating, the coated paper is subjected to drying and curing conditions in an oven at about 177°C to 204°C (350° to 400°F) for about one minute.

[0124] The kraft paper used, in the usual commercial embodiments, generally carries printed information, e.g., application instructions, suggested use, measuring scales to facilitate cutting, etc., on the non-release side.

[0125] A dimethylsiloxane homopolymer having a viscosity of about 1 to 3 Pa·s (1,000 to 3,000 cps.) (#4 spindle at 30 rpm) is mixed at a 1 to 1 weight ratio with a dimethylsiloxane-oxyalkylene block copolymer containing oxyethylene and oxypropylene units and having a viscosity of about 2.250 Pa·s (2,250 cps.) (#4 spindle at 30 rpm) to produce an admixture (hereinafter referred to as "SIL-A-23-1") which is suspended in water with a propeller type stirrer to form a composition having a ratio of polysiloxane admixture to water of about 1 to 3, respectively, by weight. This solution is slowly added to a butyl acrylate homopolymeric pressure sensitive adhesive having a solids content of about 50% by weight, a viscosity of about 0.48 Pa·s (480 cps.) (#3 spindle at 60 rpm) and a plasticity of about 1.8 mm (hereinafter referred to as "PSA-A23-1") contained in a suitable vessel fitted with a double blade mixer. The concentration of polysiloxane admixture in the pressure sensitive adhesive is 0.2% by weight based on the solids content of the adhesive. The contents of the vessel are then mixed by the double blade mixer at 60-65 rpm for 16 hours and the resulting mixture is coated onto the treated release layer by reverse roll coating. Alternatively, a 55 line quadrangular gravure roll can be used.

[0126] Thereafter, the coated release sheet is dried at about 116°C (240°F) for about 5-10 seconds to yield a dry deposit of polysiloxane modified pressure sensitive adhesive of from about 1 to 2 milligrams per square centimeter.

[0127] Finally, a polyvinyl chloride film having a thickness of about  $8.89 \times 10^{-2}$  mm (3.5 mils) is married to the thus coated release sheet by passing the combination through a nip at a pressure of about  $2.07 \times 10^5$  Pa (30 psi). The final

product is rolled into a suitable package for subsequent cutting and packaging. Sample pieces of the laminate produced by Example 1 are tested for zero minute peel, face to face peel, ease of application, etc., and are found to possess overall properties not only superior to those of a laminate produced in similar fashion but with the absence of the polysiloxane, but also to one produced from a modified adhesive in which the dimethyl silicone component is not present. The latter is evidenced by FIG. 8.

#### EXAMPLE 2

[0128] The procedure of Example 1 is followed except that instead of the polydimethylsiloxane, there is used a copolymer of a phenyl methyl dimethyl polysiloxane containing about 4.5 prime mole percent of phenyl methyl siloxane groups and having a viscosity of about 18 Pa-s (18,000 cps). (#4 spindle at 30 rpm) (the admixture is hereinafter referred to as "SIL-A23-2"). In addition, the polysiloxane material is added directly to the adhesive (PSA-1) without first suspending the polysiloxane admixture in water or other solvent and is added at a concentration of about 6% by weight based on the solids content of the adhesive.

[0129] The coating and laminating steps of Example 1 are followed and similar results are obtained.

#### EXAMPLE 3

[0130] The procedure of Example 1 is followed except that the silicone admixture disclosed therein (SIL-A23-1) is premixed with isopropyl alcohol in a ratio of about 1 to 2 respectively, by weight, and the resulting mixture is blended into an poly(butyl acrylate) homopolymeric pressure sensitive adhesive having a solids content of about 32%, a viscosity of about 0,490 Pa-s (490 cps). (#2 spindle at 30 rpm) and a plasticity of about 1.53 mm (hereinafter referred to as "PSA-A23-3"). The polysiloxane concentration is approximately 0.5% by weight based on the solids content of the adhesive.

[0131] The remaining steps of coating and laminating as described in Example 1 are followed and again similar test results were obtained.

#### EXAMPLE 4

[0132] The procedure of Example 3 is followed except that the polysiloxane (ii) used is a siloxane-oxyalkylene block copolymer having a viscosity of about 2.5 Pa-s (2500 cps). (#4 spindle at 30 rpm) (the admixture is hereinafter referred to as "SIL-A23-3").

[0133] The resulting laminate exhibits lower initial peel values than a control sample made in similar fashion but without modifying the pressure sensitive adhesive with the polysiloxane. Moreover the repositionability is improved and the ultimate adhesion to substrates is maintained when compared with a control sample which does not contain any polydimethylsiloxane component (i).

#### EXAMPLE 5

[0134] A series of laminates in accordance with the present invention are prepared using the process conditions and components and procedures set forth in Example 1. However, a series of three different polysiloxanes and three different pressure sensitive adhesives are used and the concentration of the polysiloxane in the adhesive is varied to provide three different concentrations of each polysiloxane in each pressure sensitive adhesive. The concentrations are 0.25%, 0.50% and 0.75%; each percentage of polysiloxane in the pressure sensitive adhesive being based on the dry solids weight of the pressure sensitive adhesive.

[0135] The polysiloxanes used are SIL-A23-1 of Example 1, SIL-A23-2 of Example 2, and SIL-A23-3 of Example 4. The pressure sensitive adhesives used were PSA-A23-1 of Example 1, PSA-A23-3 of Example 3, and an additional pressure sensitive adhesive (PSA-A23-2) which is a water based acrylic terpolymer pressure sensitive adhesive having a plasticity of about 3.5 mm., a viscosity of about 0.48 Pa-s (480 cps). (#3 spindle at 60 rpm) and a solids content of about 56% by weight.

[0136] For PSA-A23-1 and PSA-A23-2, the polysiloxane admixtures are added in the form of a pre-mix with water at a ratio of one part polysiloxane to three parts water. For PSA-A23-3, isopropyl alcohol is used instead of water in the same proportions.

[0137] The coating and laminating procedures of Example 1 are followed and the resulting laminates were tested for face-to-face peel, zero minute peel, 20 minute peel, 16 hour peel, and 7 day peel. The zero minute, 20 minute and 16 hour peels are determined on stainless steel, "SBR" and "ACRYLIC" surfaces. The 7 day peel value is determined only on a stainless steel surface. The results of these determinations show that the laminates prepared with the admixed silicone modified pressure sensitive compositions in accordance with the present invention are superior in terms of

their repositionability and their ultimate adhesion.

[0138] In addition to the testing of samples in accordance with the present invention, the three adhesives used are additionally tested without the addition of a polysiloxane material and act as a "Control" for comparative purposes. These control samples are prepared in an identical manner to each of the other samples except that they are not modified by the addition of a polysiloxane material. Test results indicate that the control samples are inferior to the laminates of the present invention in terms of repositionability and ultimate adhesion.

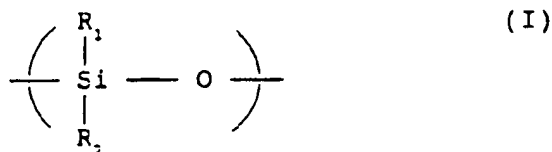
#### EXAMPLE 6

[0139] A modified pressure sensitive adhesive is prepared by dispersing SIL-A23-1 in an aqueous emulsion of a poly(2-ethylhexyl acrylate) homopolymeric pressure sensitive adhesive having a solids content of about 50% by weight, a viscosity of about 0.48 Pa·s (480 cps). (#3 spindle at 60 rpm) and a plasticity of about 1.8 mm (hereinafter referred to as PSA-A23-4). The concentration of SIL-A23-1 in PSA-A23-4 is about 0.75% based on the dry solids weight of the adhesive. The modified pressure sensitive adhesive is direct coated onto a polyvinyl chloride film having a thickness of about  $8.89 \cdot 10^{-2}$  mm (3.5 mils) by a 55 line quadrangular gravure roll to an average thickness of about  $1.27 \cdot 10^{-2}$  mm (0.5 mil) and a dry deposit of about 1.6 mg/cm<sup>2</sup>. The resulting laminate is married to a release sheet prepared from kraft paper (19.05 kg (42 pounds) per ream) coated with a conventional silicone release finish. Upon stripping the release film from the laminate a product is obtained exhibiting relatively low face-to-face peel and possessing overall properties superior to those of a laminate produced in similar fashion but with the absence of the polysiloxane modification of the pressure sensitive adhesive.

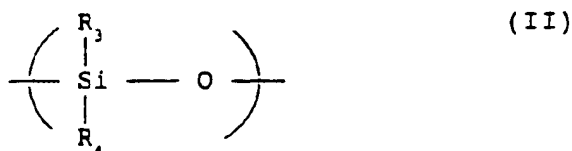
[0140] By varying the concentration of admixed polysiloxanes in the adhesive one can reduce the adhesion force upon initial application but not sacrifice too much of the ultimate adhesion to the bonding substrate.

#### Claims

1. An improved method for making a laminate comprising coating a first sheet having a release surface thereon with a modified pressure sensitive adhesive to form a first laminate, subjecting said first laminate to conditions suitable to dry or cure the pressure sensitive adhesive, and marrying the pressure sensitive adhesive side of the thus treated first laminate to the inner surface of a facing layer having inner and outer surfaces; said modified pressure sensitive adhesive comprising a pressure sensitive adhesive and an admixture of polysiloxanes (i) and (ii) in intimate combination with the pressure sensitive adhesive, in an amount of 0.001 to 20.0 percent based on the solids content of the pressure sensitive adhesive, said polysiloxane (i) being substantially water insoluble and insoluble in said pressure sensitive adhesive and formed from monomeric units having structures (I) and (II) as follows:



and

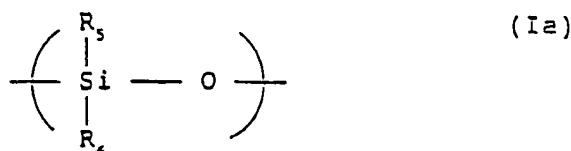


wherein  $R_1$  is methyl, ethyl, phenyl, tolyl, or a mixture of any of them,  $R_2$  is methyl, ethyl or phenyl; and  $R_3$  and  $R_4$  are the same or different and are methyl or ethyl, wherein the majority of units (I) and (II) comprise units (II), and said polysiloxane (i) has a viscosity in the range of from 0.005 to 60 Pa·s (5 cps to 60,000 cps) measured at 25°C

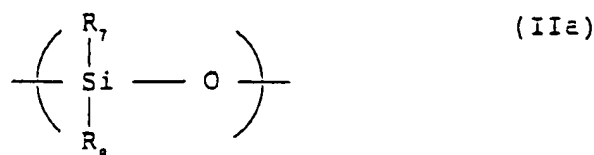


with a #4 spindle at 30 rpm; and

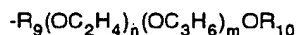
said polysiloxane (ii) being water-soluble and compatible with polysiloxane (i) and formed monomeric units having structures (Ia) and (IIa) as follows:



and

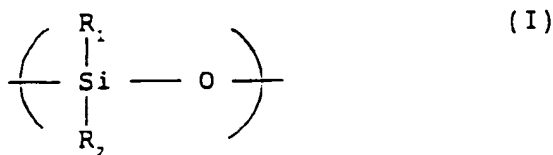


wherein  $R_5$  is a polyoxyalkylene group having the structural formula

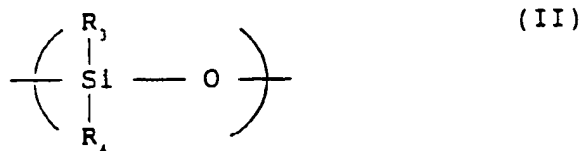


wherein  $R_{10}$  is hydrogen or a monovalent hydrocarbon group having from 1 to 10 carbon atoms and  $R_5$  contains both oxyethylene and oxypropylene units,  $R_9$  is an alkylene group having at least two carbon atoms,  $n$  and  $m$  are numbers, the sum of  $n$  and  $m$  is at least 1 and the oxyalkylene unit  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$  has a molecular weight of at least 80, and wherein there are at least two units having structure (Ia) and at least 3 units having structure (IIa) and wherein the oxyalkylene unit constitutes from 85 to 30 weight percent of the polysiloxane polymer;  $R_6$  may be methyl, ethyl or phenyl; and  $R_7$  and  $R_8$  may be the same or different and may be methyl or ethyl, and said polysiloxane (ii) has a viscosity range of from 0.05 to 5 Pa·s (50 to 5000 cps) measured at 25°C with a #4 spindle at 30 rpm, the amount of polysiloxane (i) in said admixture being effective to separate from the adhesive and to bloom to the adhesive/air interface of said first laminate coated with said adhesive composition to provide enhanced repositionability and the amount of polysiloxane (ii) in said admixture being effective to provide improved wet-out of the adhesive to a bonding substrate and, ultimately, improved adhesion thereto.

2. An improved method for making a laminate comprising coating a facing layer having outer and inner surfaces with a layer of a modified pressure sensitive adhesive to form a first laminate, subjecting said first laminate to conditions suitable to dry or cure the pressure sensitive adhesive, and marrying the pressure sensitive adhesive side of the thus treated first laminate to a release surface; said modified pressure sensitive adhesive comprising a pressure sensitive adhesive and an admixture of polysiloxanes (i) and (ii) in intimate combination with the pressure sensitive adhesive, in an amount of 0.001 to 20.0 percent based on the solids content of the pressure sensitive adhesive, said polysiloxane (i) being substantially water-soluble and insoluble in said pressure sensitive adhesive and formed from monomeric units having structures (I) and (II) as follows:

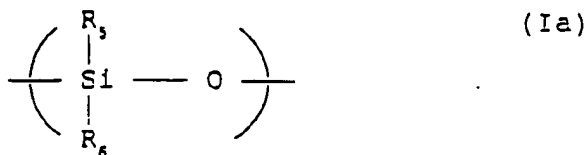


and

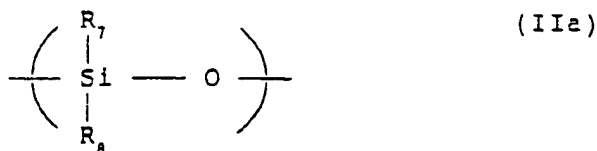


wherein  $R_1$  is methyl, ethyl, phenyl, tolyl, or a mixture of any of them,  $R_2$  is methyl, ethyl or phenyl; and  $R_3$  and  $R_4$  are the same or different and are methyl or ethyl, wherein the majority of units (I) and (II) comprise units (II), and said polysiloxane (i) has a viscosity in the range of from 0.005 to 60 Pa·s (5 cps to 60,000 cps) measured at 25°C with a #4 spindle at 30 rpm; and

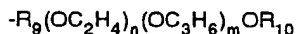
said polysiloxane (ii) being water-soluble and compatible with polysiloxane (i) and formed monomeric units having structures (Ia) and (IIa) as follows:



and



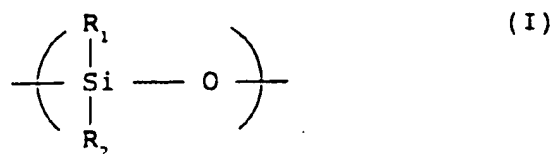
wherein  $R_6$  is a polyoxyalkylene group having the structural formula



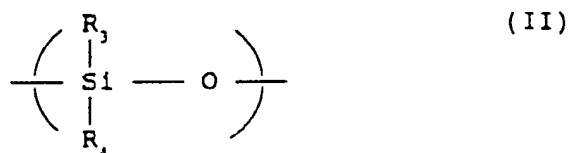
wherein  $R_{10}$  is hydrogen or a monovalent hydrocarbon group having from 1 to 10 carbon atoms and  $R_9$  contains both oxyethylene and oxypropylene units,  $R_9$  is an alkylene group having at least two carbon atoms,  $n$  and  $m$  are numbers, the sum of  $n$  and  $m$  is at least 1 and the oxyalkylene unit  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$  has a molecular weight of at least 80, and wherein there are at least two units having structure (Ia) and at least 3 units having structure (IIa) and wherein the oxyalkylene unit constitutes from 85 to 30 weight percent of the polysiloxane polymer;  $R_6$  may be either methyl, ethyl or phenyl; and  $R_7$  and  $R_8$  may be the same or different and may be methyl or ethyl, and said polysiloxane (ii) has a viscosity range of from 0.05 to 5 Pa·s (50 to 5000 cps) measured at 25°C with a #4 spindle at 30 rpm, the amount of polysiloxane (i) in said admixture being effective to separate from the adhesive and to bloom to the adhesive/air interface of said first laminate coated with said adhesive composition to provide enhanced repositionability and the amount of polysiloxane (ii) in said admixture being effective to provide improved wet-out of the adhesive to a bonding substrate and, ultimately, improved adhesion thereto.

3. A laminate made according to the method in claim 1 or 2.
4. A pressure sensitive adhesive composition comprising a pressure sensitive adhesive and 0.001 to 20 percent based on the solids content of the pressure sensitive adhesive of an admixture of polysiloxanes (i) and (ii),

said polysiloxane (i) being substantially water-insoluble and insoluble in said pressure sensitive adhesive and formed from monomeric units having structures (I) and (II) as follows:

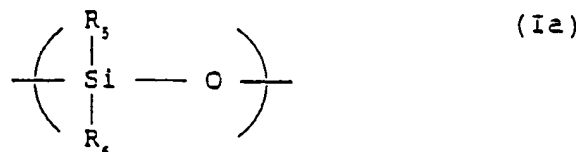


and

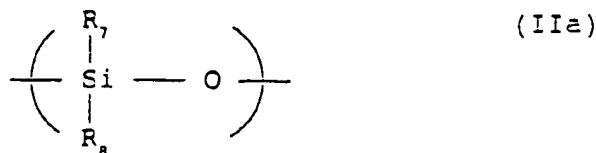


wherein  $R_1$  is methyl, ethyl, phenyl, tolyl, or a mixture of any of them,  $R_2$  is methyl, ethyl or phenyl; and  $R_3$  and  $R_4$  are the same or different and are methyl or ethyl, wherein the majority of units (I) and (II) comprise units (II), and said polysiloxane (i) has a viscosity in the range of from 0.005 to 60 Pa·s (5 cps to 60,000 cps) measured at 25°C with a #4 spindle at 30 rpm; and

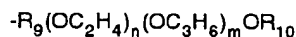
said polysiloxane (ii) being water-soluble and compatible with polysiloxane (i) and formed monomeric units having structures (Ia) and (IIa) as follows:



and



wherein  $R_5$  is a polyoxyalkylene group having the structural formula

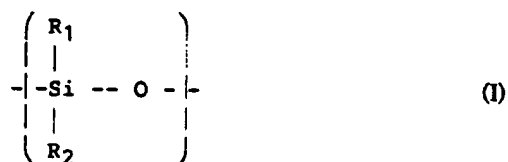


wherein  $R_{10}$  is hydrogen or a monovalent hydrocarbon group having from 1 to 10 carbon atoms and  $R_9$  contains both oxyethylene and oxypropylene units,  $R_9$  is an alkylene group having at least two carbon atoms,  $n$  and  $m$  are numbers, the sum of  $n$  and  $m$  is at least 1 and the oxyalkylene unit  $R_{10}(\text{OC}_3\text{H}_6)_m(\text{OC}_2\text{H}_4)_n$ , has a molecular weight of at least 80, and wherein there are at least two units having structure (Ia) and at least 3 units having structure

(IIa) and wherein the oxyalkylene unit constitutes from 85 to 30 weight percent of the polysiloxane polymer;  $R_6$  may be either methyl, ethyl or phenyl; and  $R_7$  and  $R_8$  may be the same or different and may be methyl or ethyl, and said polysiloxane (ii) has a viscosity range of from 0.05 to 5 Pa·s (50 to 5000 cps) measured at 25°C with a #4 spindle at 30 rpm, the amount of polysiloxane (i) in said admixture being effective to separate from the adhesive and to bloom to the adhesive/air interface of said first laminate coated with said adhesive composition to provide enhanced repositionability and the amount of polysiloxane (ii) in said admixture being effective to provide improved wet-out of the adhesive to a bonding substrate and, ultimately, improved adhesion thereto.

## Patentansprüche

1. Verbessertes Verfahren zum Herstellen eines Laminates, umfassend das Überziehen einer ersten Folie, die eine Trennoberfläche darauf hat, mit einem modifizierten Haftkleber zur Bildung eines ersten Laminates, Aussetzen des ersten Laminates gegenüber Bedingungen, die zum Trocknen oder Härten des Haftklebers geeignet sind und Vereinen der Haftkleber-Seite des so behandelten ersten Laminates mit der inneren Oberfläche einer Deckschicht mit innerer und äußerer Oberfläche, wobei der modifizierte Haftkleber einen Haftkleber und eine Mischung der Polysiloxane (i) und (ii) in inniger Kombination mit dem Haftkleber in einer Menge von 0,001 bis 20,0%, bezogen auf den Feststoffgehalt des Haftklebers, umfaßt, das Polysiloxan (i) im wesentlichen in Wasser unlöslich und in dem Haftkleber unlöslich ist und gebildet ist aus Monomeren-Einheiten mit den folgenden Strukturen (I) und (II):



und



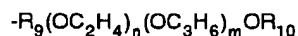
worin  $R_1$  Methyl, Ethyl, Phenyl, TolyI oder eine Mischung irgendwelcher dieser Reste ist,  $R_2$  Methyl, Ethyl oder Phenyl ist, und  $R_3$  und  $R_4$  gleich oder verschieden und Methyl oder Ethyl sind, wobei die Mehrzahl der Einheiten (I) und (II) Einheiten (II) umfaßt, und das Polysiloxan (i) eine Viskosität im Bereich von 0,005 bis 60 Pa·s (5 cps bis 60.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, hat und das Polysiloxan (ii) wasserlöslich und verträglich mit dem Polysiloxan (i) und aus monomeren Einheiten der folgenden Strukturen (Ia) und (IIa) gebildet ist:



und



worin  $R_8$  eine Polyoxyalkylengruppe der Strukturformel ist

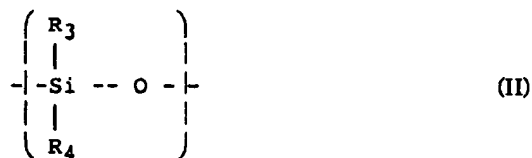


worin  $R_{10}$  Wasserstoff oder eine einwertige Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen ist und  $R_9$  sowohl Oxyethylen- als auch Oxypropylen-Einheiten enthält,  $R_9$  eine Alkylengruppe mit mindestens 2 Kohlenstoffatomen ist,  $n$  und  $m$  Zahlen sind, deren Summe mindestens 1 ist und die Oxyalkylen-Einheit  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$  ein Molekulargewicht von mindestens 80 aufweist, und worin es mindestens 2 Einheiten mit der Struktur (Ia) und mindestens 3 Einheiten mit der Struktur (IIa) gibt, die Oxyalkylen-Einheit von 85 bis 30 Gew.-% des Polysiloxanpolymers ausmacht,  $R_6$  Methyl, Ethyl oder Phenyl sein kann und  $R_7$  und  $R_8$  gleich oder verschieden und Methyl oder Ethyl sein können und das Polysiloxan (ii) einen Viskositätsbereich von 0,05 bis 5 Pa.s (50-5.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, aufweist, die Menge des Polysiloxans (i) in der Mischung wirksam ist, um sich vom Kleber zu trennen und an der Klebstoff/ Luft-Grenzfläche des ersten Laminates, das mit der Klebstoff-Zusammensetzung überzogen ist, auszublühen, um eine verbesserte Wiederanordnung zu schaffen, und die Menge des Polysiloxans (ii) in der Mischung wirksam ist, um ein verbessertes Benetzen des Klebstoffes an einem Binde substrat und schließlich eine verbesserte Haftung daran zu schaffen.

2. Verbessertes Verfahren zum Herstellen eines Laminates, umfassend das Überziehen einer Deckschicht mit äußerer und innerer Oberfläche mit einer Schicht aus einem modifizierten Haftkleber zur Bildung eines ersten Laminates, Aussetzen des ersten Laminates gegenüber Bedingungen, die zum Trocknen oder Härten des Haftklebers geeignet sind, und Vereinigen der Haftkleber-Seite des so behandelten ersten Laminates mit einer Trennoberfläche, wobei der modifizierte Haftkleber einen Haftkleber und eine Mischung von Polysiloxanen (i) und (ii) in inniger Kombination mit dem Haftkleber in einer Menge von 0,001 bis 20,0%, bezogen auf den Feststoffgehalt des Haftklebers, umfaßt, das Polysiloxan (i) im wesentlichen wasserlöslich und unlöslich in dem Haftkleber ist und gebildet ist aus monomeren Einheiten der folgenden Strukturen (I) und (II):

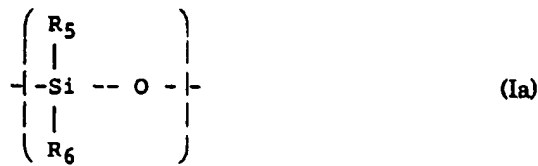


und



worin  $R_1$  Methyl, Ethyl, Phenyl, TolyI oder eine Mischung irgendwelcher dieser Reste ist,  $R_2$  Methyl, Ethyl oder Phenyl ist, und  $R_3$  und  $R_4$  gleich oder verschieden und Methyl oder Ethyl sind, wobei die Mehrzahl der Einheiten (I) und (II) Einheiten (II) umfaßt, und das Polysiloxan (i) eine Viskosität im Bereich von 0,005 bis 60 Pa.s (5 cps bis 60.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, hat und das Polysiloxan (ii) wasserlöslich

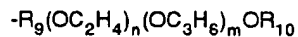
und verträglich mit dem Polysiloxan (i) und aus monomeren Einheiten der folgenden Strukturen (Ia) und (IIa) gebildet ist:



und



worin  $R_5$  eine Polyoxyalkylengruppe der Strukturformel ist



worin  $R_{10}$  Wasserstoff oder eine einwertige Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen ist und  $R_5$  sowohl Oxyethylen- als auch Oxypropylen-Einheiten enthält,  $R_9$  eine Alkylengruppe mit mindestens 2 Kohlenstoffatomen ist,  $n$  und  $m$  Zahlen sind, deren Summe mindestens 1 ist und die Oxyalkylen-Einheit  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$  ein Molekulargewicht von mindestens 80 aufweist, und worin es mindestens 2 Einheiten mit der Struktur (Ia) und mindestens 3 Einheiten mit der Struktur (IIa) gibt, die Oxyalkylen-Einheit von 85 bis 30 Gew.-% des Polysiloxanpolymers ausmacht,  $R_6$  Methyl, Ethyl oder Phenyl sein kann und  $R_7$  und  $R_8$  gleich oder verschieden und Methyl oder Ethyl sein können und das Polysiloxan (ii) einen Viskositätsbereich von 0,05 bis 5 Pa·s (50-5.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, aufweist, die Menge des Polysiloxans (i) in der Mischung wirksam ist, um sich vom Klebstoff zu trennen und an der Klebstoff/Luft-Grenzfläche des ersten Laminates, das mit der Klebstoff-Zusammensetzung überzogen ist, auszublühen, um eine verbesserte Wiederanordnung zu schaffen, und die Menge des Polysiloxans (ii) in der Mischung wirksam ist, um ein verbessertes Benetzen des Klebstoffes an einem Bindesubstrat und schließlich eine verbesserte Haftung daran zu schaffen.

3. Laminat, hergestellt nach dem Verfahren in Anspruch 1 oder 2.
4. Haftkleber-Zusammensetzung, umfassend einen Haftkleber und 0,001 bis 20%, bezogen auf den Feststoffgehalt des Haftklebers, von einer Mischung von Polysiloxanen (i) und (ii), wobei das Polysiloxan (i) im wesentlichen wasserunlöslich ist und unlöslich ist in dem Haftkleber und gebildet ist aus monomeren Einheiten der folgenden Strukturen (I) und (II):



und



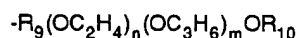
worin  $R_1$  Methyl, Ethyl, Phenyl, TolyI oder eine Mischung irgendwelcher dieser Reste ist,  $R_2$  Methyl, Ethyl oder Phenyl ist, und  $R_3$  und  $R_4$  gleich oder verschieden und Methyl oder Ethyl sind, wobei die Mehrzahl der Einheiten (I) und (II) Einheiten (II) umfaßt, und das Polysiloxan (i) eine Viskosität im Bereich von 0,005 bis 60 Pa·s (5 cps bis 60.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, hat und das Polysiloxan (ii) wasserlöslich und verträglich mit dem Polysiloxan (i) und aus monomeren Einheiten der folgenden Strukturen (Ia) und (IIa) gebildet ist:



und



worin  $R_5$  eine Polyoxyalkylengruppe der Strukturformel ist



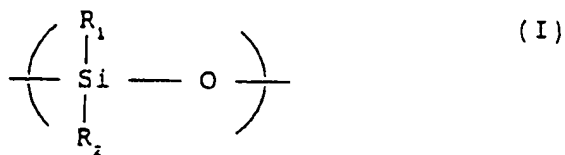
worin  $R_{10}$  Wasserstoff oder eine einwertige Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen ist und  $R_9$  sowohl Oxyethylen- als auch Oxypropylen-Einheiten enthält,  $R_9$  eine Alkylengruppe mit mindestens 2 Kohlenstoffatomen ist,  $n$  und  $m$  Zahlen sind, deren Summe mindestens 1 ist und die Oxyalkylen-Einheit  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$  ein Molekulargewicht von mindestens 80 aufweist, und worin es mindestens 2 Einheiten mit der Struktur (Ia) und mindestens 3 Einheiten mit der Struktur (IIa) gibt, die Oxyalkylen-Einheit von 85 bis 90 Gew.-% des Polysiloxanpolymers ausmacht,  $R_6$  Methyl, Ethyl oder Phenyl sein kann und  $R_7$  und  $R_8$  gleich oder verschieden und Methyl oder Ethyl sein können, und das Polysiloxan (ii) einen Viskositätsbereich von 0,05 bis 5 Pa·s (50-5.000 cps), gemessen bei 25°C mit einer Spindel Nr. 4 bei 30 U/min, aufweist, die Menge des Polysiloxans (i) in der Mischung wirksam ist, um sich vom Kleber zu trennen und an der Klebstoff/Luft-Grenzfläche des ersten Laminates, das mit der Klebstoff-Zusammensetzung überzogen ist, auszublühen, um eine verbesserte Wiederanordnung zu schaffen, und die Menge des Polysiloxans (ii) in der Mischung wirksam ist, um ein verbessertes Benetzen des Klebstoffes an einem Bindesubstrat und schließlich eine verbesserte Haftung daran zu schaffen.

#### Revendications

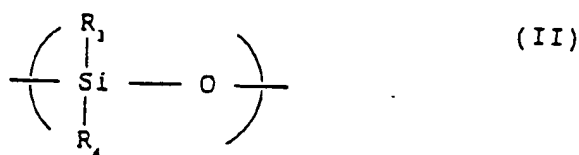
1. Procédé amélioré pour fabriquer un stratifié, qui comprend l'application sur une première feuille ayant une surface anti-adhésive d'un adhésif de contact modifié pour former un premier stratifié, l'opération consistant à soumettre ledit premier stratifié à des conditions convenant au séchage ou au durcissement de l'adhésif de contact, et la réunion de la face portant l'adhésif de contact du premier stratifié ainsi traité à la surface intérieure d'une couche

de revêtement possédant une surface intérieure et une surface extérieure; ledit adhésif de contact modifié comprenant un adhésif de contact et un mélange de polysiloxanes (i) et (ii) en combinaison intime avec l'adhésif de contact, en une quantité de 0,001 à 20,0 % en poids par rapport à l'extrait sec de l'adhésif de contact,

ledit polysiloxane (i) étant essentiellement insoluble dans l'eau et insoluble dans ledit adhésif de contact, et étant formé de motifs monomères ayant les structures (I) et (II) ci-après :

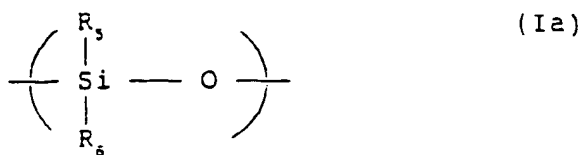


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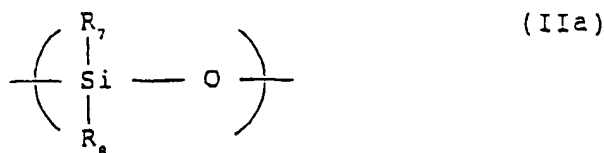


où  $R_1$  est méthyle, éthyle, phényle, tolyle ou un mélange de n'importe lesquels d'entre eux,  $R_2$  est méthyle, éthyle ou phényle ; et  $R_3$  et  $R_4$  sont identiques ou différents et représentent méthyle ou éthyle, où les motifs (I) et (II) comprennent majoritairement des motifs (II), et ledit polysiloxane (i) a une viscosité de 0,005 à 60 Pa.s (5 à 60 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute ; et

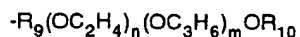
ledit polysiloxane (ii) étant soluble dans l'eau et compatible avec le polysiloxane (i) et étant constitué de motifs monomères ayant les structures (Ia) et (IIa) ci-après :



et



où  $R_5$  est un groupe polyoxyalkylène ayant la formule développée :



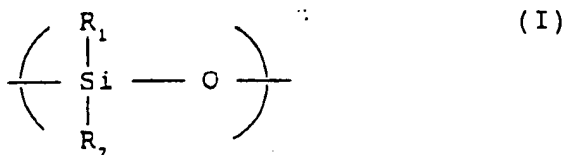
dans laquelle  $R_{10}$  est hydrogène ou un groupe hydrocarboné monovalent ayant de 1 à 10 atomes de carbone, et  $R_9$  contient tant des motifs oxyéthylène que des motifs oxypropylène,  $R_9$  est un groupe alkylène ayant au moins deux atomes de carbone, n et m sont des nombres tels que la somme de n et de m soit d'au moins 1 et le motif



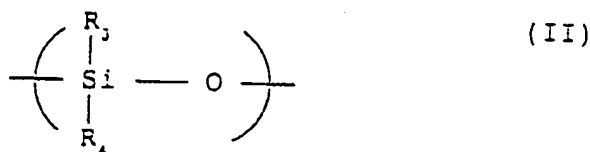
oxyalkylène  $R_{10}(OC_3H_6)_m(OC_2H_4)_n$ , a une masse moléculaire d'au moins 80, et où il y a au moins deux motifs ayant la structure (Ia) et au moins trois motifs ayant la structure (IIa), et où le motif oxyalkylène constitue de 85 à 30 % en poids du polymère polysiloxane ;  $R_6$  peut être méthyle, éthyle, ou phényle ; et  $R_7$  et  $R_8$  peuvent être identiques ou différents et peuvent être méthyle ou éthyle, et ledit polysiloxane (ii) a une viscosité de 0,05 à 5 Pa.s (50 à 5 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute, la quantité du polysiloxane (i) dans ledit mélange étant suffisante pour se séparer de l'adhésif et pour migrer vers l'interface adhésif/air d'un article revêtu de ladite composition adhésive, pour assurer une bonne aptitude au repositionnement, et la quantité du polysiloxane (ii) dans ledit mélange étant suffisante pour assurer un mouillage amélioré de l'adhésif sur un substrat collé, et finalement une meilleure adhérence à ce dernier.

2. Procédé amélioré pour fabriquer un stratifié, qui comprend l'application sur une couche de revêtement ayant une surface extérieure et une surface intérieure d'une couche d'un adhésif de contact modifié pour former un premier stratifié, l'opération consistant à soumettre ledit premier stratifié à des conditions convenant au séchage ou au durcissement de l'adhésif de contact, et la réunion à une surface anti-adhésive de la face portant l'adhésif de contact du premier stratifié ainsi obtenu ; ledit adhésif de contact modifié comprenant un adhésif de contact et un mélange de polysiloxanes (i) et (ii) en combinaison intime avec l'adhésif de contact, en une quantité de 0,001 à 20,0 % en poids par rapport à l'extrait sec de l'adhésif de contact,

ledit polysiloxane (i) étant essentiellement insoluble dans l'eau et insoluble dans ledit adhésif de contact, et étant formé de motifs monomères ayant les structures (I) et (II) ci-après :

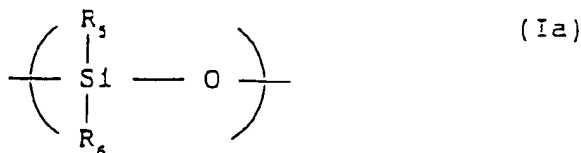


et

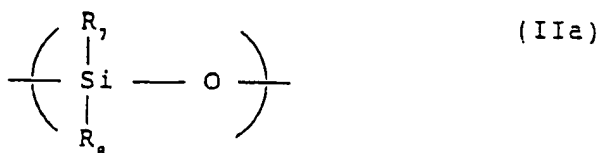


où  $R_1$  est méthyle, éthyle, phényle, tolyle ou un mélange de n'importe lesquels d'entre eux,  $R_2$  est méthyle, éthyle ou phényle ; et  $R_3$  et  $R_4$  sont identiques ou différents et représentent méthyle ou éthyle, où les motifs (I) et (II) sont majoritairement des motifs (II), et ledit polysiloxane (i) a une viscosité de 0,005 à 60 Pa.s (5 à 60 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute ; et

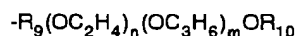
ledit polysiloxane (ii) étant soluble dans l'eau et compatible avec le polysiloxane (i) et étant constitué de motifs monomères ayant les structures (Ia) et (IIa) ci-après :



et



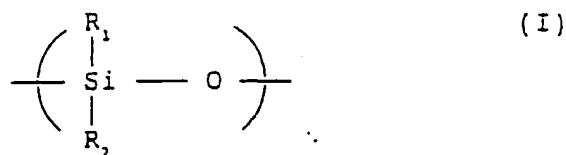
où  $R_5$  est un groupe polyoxyalkylène ayant la formule développée :



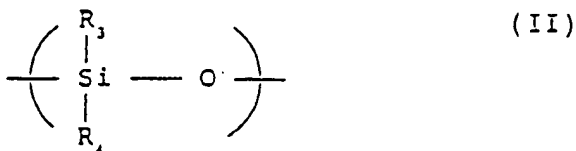
dans laquelle  $R_{10}$  est hydrogène ou un groupe hydrocarboné monovalent ayant de 1 à 10 atomes de carbones, et  $R_9$  contient tant des motifs oxyéthylène que des motifs oxypropylène,  $R_9$  est un groupe alkylène ayant au moins deux atomes de carbone,  $n$  et  $m$  sont des nombres tels que la somme de  $n$  et de  $m$  soit d'au moins 1 et le motif oxyalkylène  $R_{10}(\text{OC}_3\text{H}_6)_m(\text{OC}_2\text{H}_4)_n$ , a une masse moléculaire d'au moins 80, et où il y a au moins deux motifs ayant la structure (Ia) et au moins trois motifs ayant la structure (IIa), et où le motif oxyalkylène constitue de 85 à 30 % en poids du polymère polysiloxane ;  $R_6$  peut être méthyle, éthyle, ou phényle ; et  $R_7$  et  $R_8$  peuvent être identiques ou différents et peuvent être méthyle ou éthyle, et ledit polysiloxane (ii) a une viscosité de 0,05 à 5 Pa.s (50 à 5 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute, la quantité du polysiloxane (i) dans ledit mélange étant suffisante pour se séparer de l'adhésif et pour migrer vers l'interface adhésif/air d'un article revêtu de ladite composition adhésive, pour assurer une bonne aptitude au repositionnement, et la quantité du polysiloxane (ii) dans ledit mélange étant suffisante pour assurer un mouillage amélioré de l'adhésif sur un substrat collé, et finalement une meilleure adhérence à ce dernier.

3. Stratifié fabriqué par le procédé selon la revendication 1 ou 2.

4. Composition d'adhésif de contact comprenant un adhésif de contact et de 0,001 à 20 %, par rapport à l'extrait sec de l'adhésif de contact, d'un mélange de polysiloxanes (i) et (ii),  
ledit polysiloxane (i) étant essentiellement insoluble dans l'eau et insoluble dans ledit adhésif de contact, et étant formé de motifs monomères ayant les structures (I) et (II) ci-après :

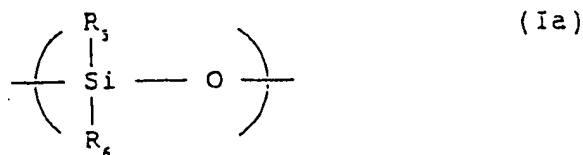


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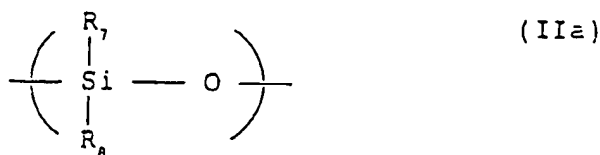


où  $R_1$  est méthyle, éthyle, phényle, tolyle ou un mélange de n'importe lesquels d'entre eux,  $R_2$  est méthyle, éthyle ou phényle ; et  $R_3$  et  $R_4$  sont identiques ou différents et représentent méthyle ou éthyle, où les motifs (I) et (II) sont majoritairement des motifs (II), et ledit polysiloxane (i) a une viscosité de 0,005 à 60 Pa.s (5 à 60 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute ; et

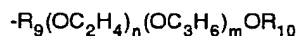
ledit polysiloxane (ii) étant soluble dans l'eau et compatible avec le polysiloxane (i) et étant constitué de motifs monomères ayant les structures (Ia) et (IIa) ci-après:



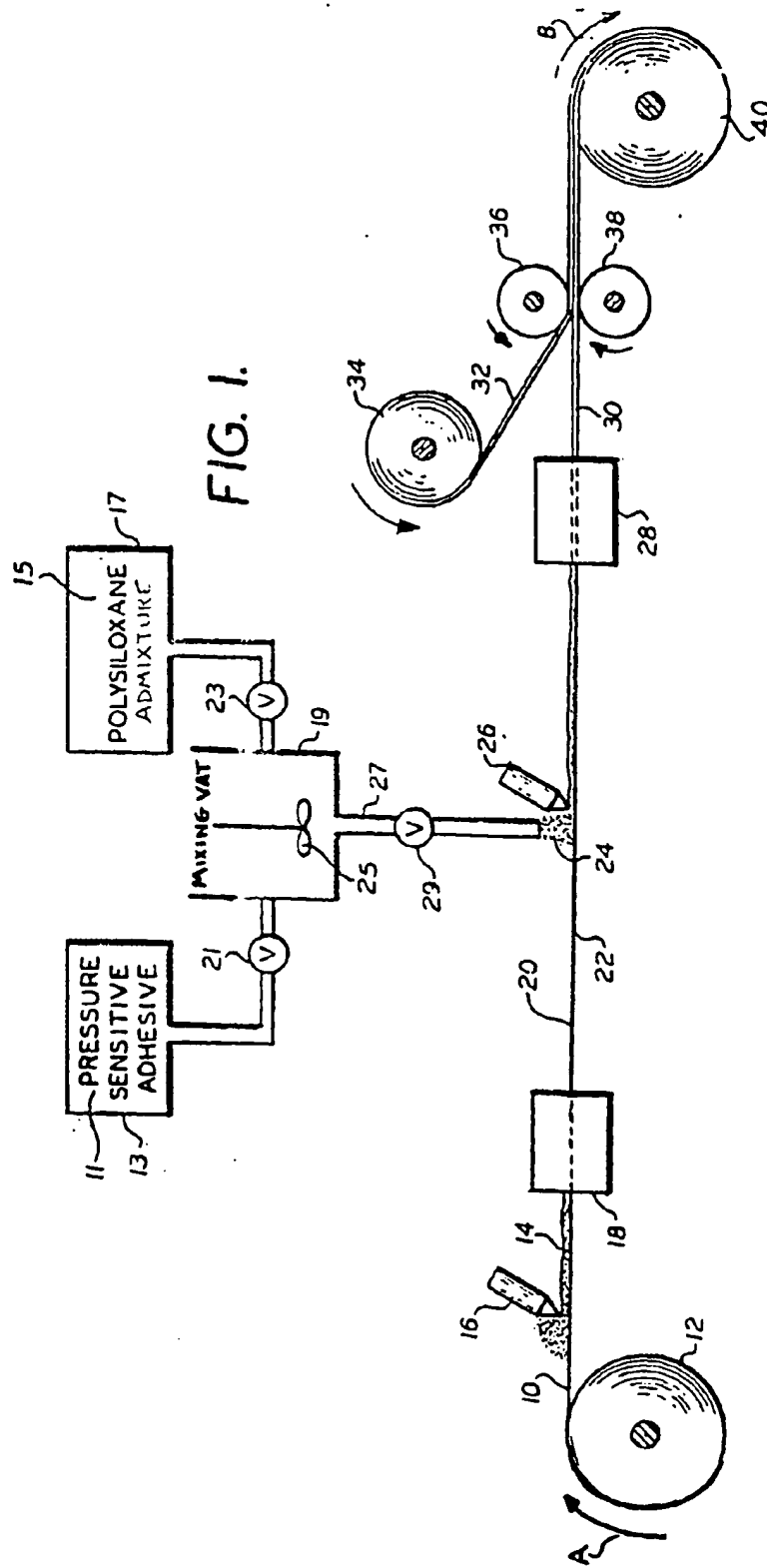
et



où  $R_6$  est un groupe polyoxyalkylène ayant la formule développée :



dans laquelle  $R_{10}$  est hydrogène ou un groupe hydrocarboné monovalent ayant de 1 à 10 atomes de carbone, et  $R_9$  contient tant des motifs oxyéthylène que des motifs oxypropylène,  $R_9$  est un groupe alkylène ayant au moins deux atomes de carbone,  $n$  et  $m$  sont des nombres tels que la somme de  $n$  et de  $m$  soit d'au moins 1 et le motif oxyalkylène  $R_{10}$   $(\text{OC}_3\text{H}_6)_m(\text{OC}_2\text{H}_4)_n$ , a une masse moléculaire d'au moins 80, et où il y a au moins deux motifs ayant la structure (Ia) et au moins trois motifs ayant la structure (IIa), et où le motif oxyalkylène constitue de 85 à 30 % en poids du polymère polysiloxane ;  $R_6$  peut être méthyle, éthyle, ou phényle ; et  $R_7$  et  $R_8$  peuvent être identiques ou différents et peuvent être méthyle ou éthyle, et ledit polysiloxane (ii) a une viscosité 0,05 à 5 Pa.s (50 et 5 000 cP), mesurée à 25°C avec une broche n°4 à 30 tours par minute, la quantité du polysiloxane (i) dans ledit mélange étant suffisante pour se séparer de l'adhésif et pour migrer vers l'interface adhésif/air d'un article revêtu de ladite composition adhésive, pour assurer une bonne aptitude au repositionnement, et la quantité du polysiloxane (ii) dans ledit mélange étant suffisante pour assurer un mouillage amélioré de l'adhésif sur un substrat collé, et finalement une meilleure adhérence à ce dernier.



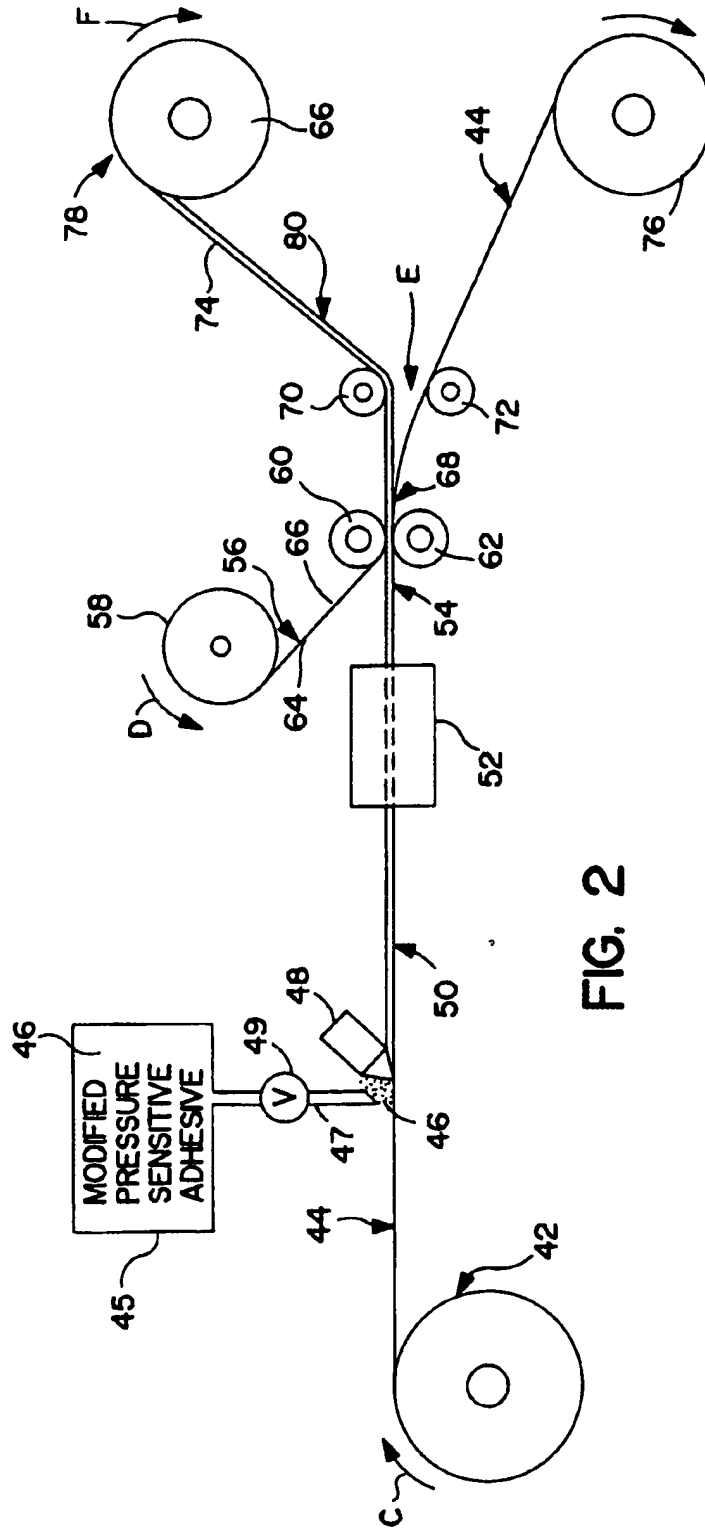


FIG. 2

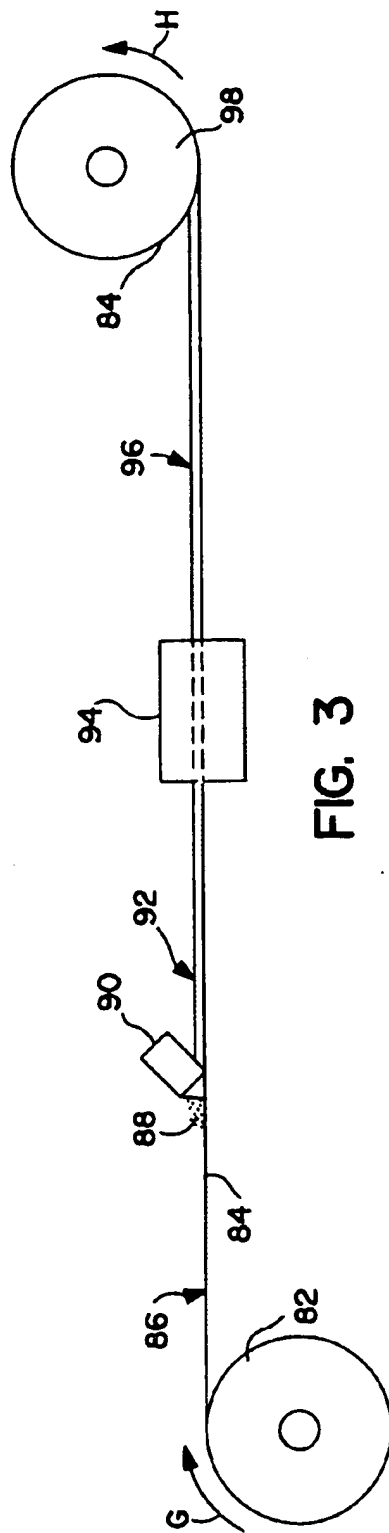


FIG. 3

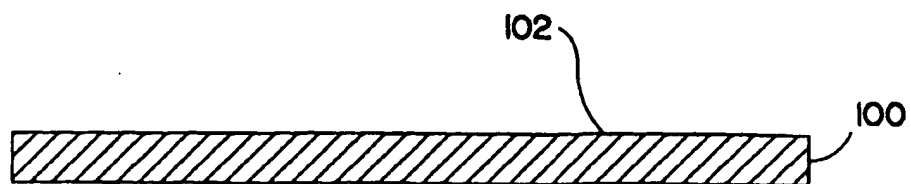


FIG. 4

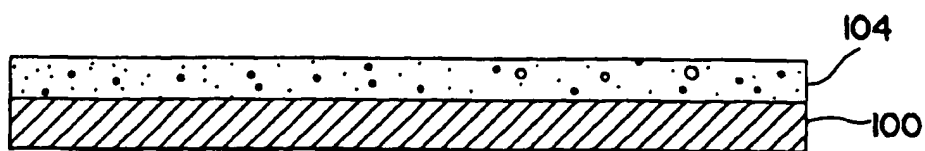


FIG. 5

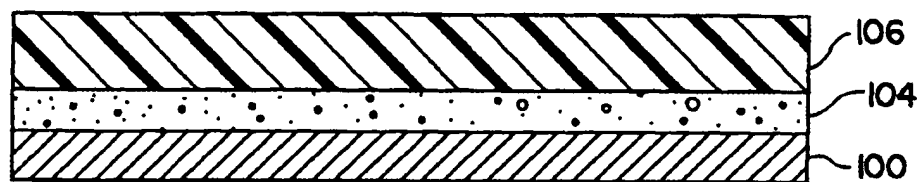


FIG. 6

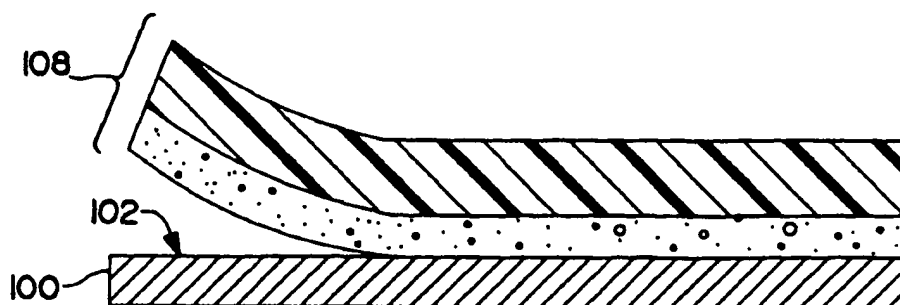


FIG. 7

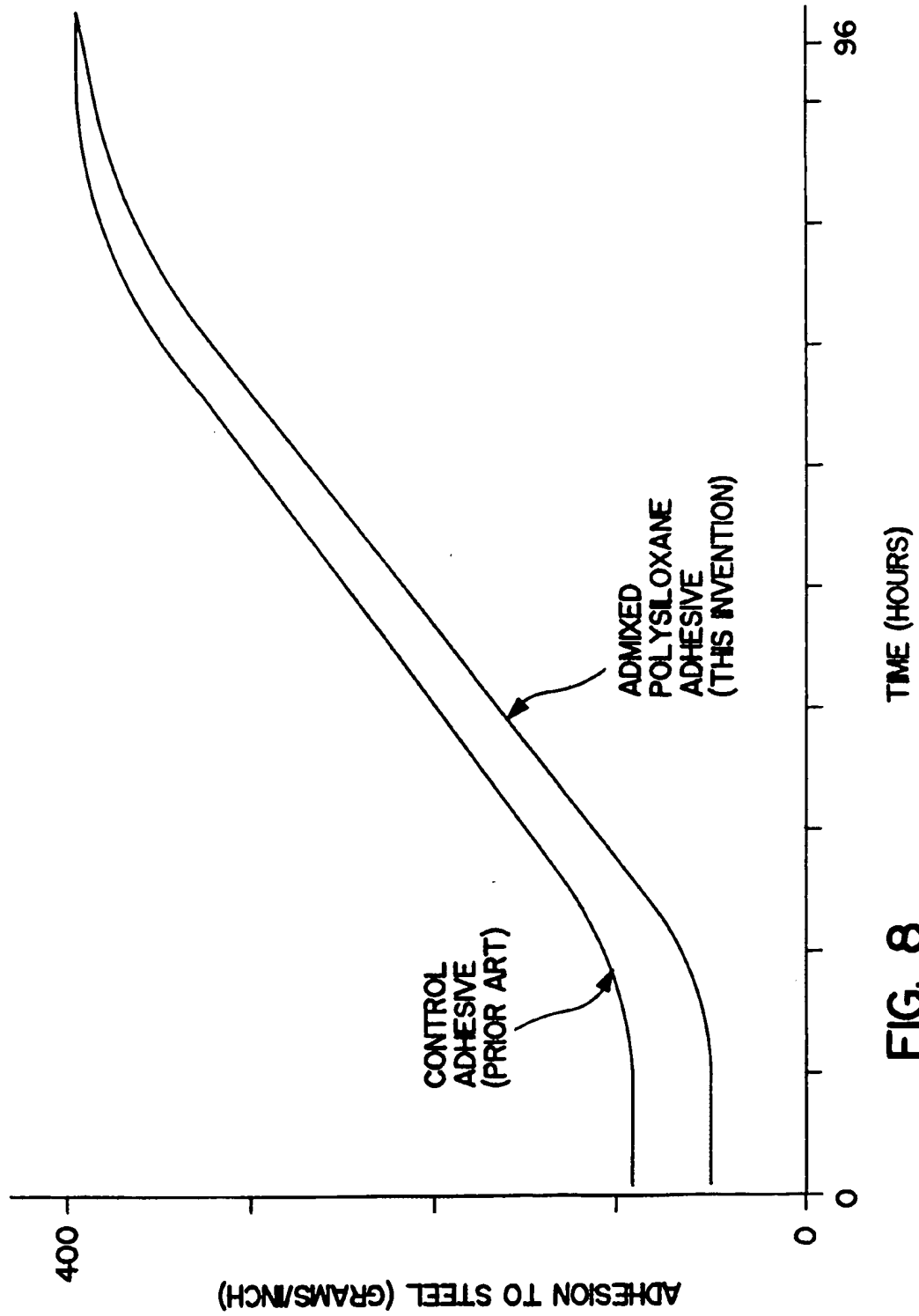


FIG. 8